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Studies on Canned Tuna in Oils. (I)

1. Chemical studies on heating, storing and mixing of Oils.
2. Acid values and iodine values of Oils in canned tuna in Oils.

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Olive oil, arachis oil and cottonseed oil used for canning various foods in them improve by degrees the taste and flavour of the canned contents while they are kept intact. This phenomenon is called "ripeness". It is said that the canned sardine in oil in France reaches to the maximum ripeness in 9～18 months after manufacturing, whereas that in Portugal in 6～9 months.

T. ONO and N. SUZUKI[1] made an extensive study of the ripeness of the canned sardine in oil in Japan. The present paper deals with chemical studies on the oils used for canning tuna in them, the results being obtained with the following methods.

Sample oil was dissolved in the mixture of alcohol and ether (1 : 2), and was titrated with $\frac{N}{10}KOH$ alcoholic solution using phenolphthalein as indicator to determine the acid value. Iodine value was determined by Wijs' method.

(1) Jl. of the Imperial Fisheries Institute, Vol. 13, No. 1, 1917.

(I) Chemical studies on heating, storing and mixing of Oils.

1. Acid values and iodine values of oils heated and kept intact after packed in cans.

It[2), 3)] has been reported that though the qualities of oils slightly change when heated in the air below the temperature of 270°C for thirty minutes, they remarkably change above the temperature of 270°C.

T. ONO and N. SUZUKI[4)] published the report that though the characteristics of olive oil and other vegetable oils changed when heated in the air at 110°~120°C for three hours, they did not change when the oils were packed in cans and then heated at 100°C for two hours. Many investigations concerning the changes of oils during storage have been made. It has been published[5), 6)] that the change of the acid values of vegetable oils and fish oils takes place, but that of iodine values is slight or completely absent in the air during storage.

We have carried out the the following experiments.

Cottonseed oil, soya bean oil, olive oil and tuna oil were respectively packed in cans fully with little or no head space in the can, (a) heated at 116.5°C for $2\frac{1}{2}$ hours and examined soon after cooling (b) heated at 110°C, 113°C and 115.2°C for $1\frac{1}{3}$ hours respectively after canning and were kept intact for 700 days before examination. On the other hand each original unheated oil packed in glass bottle and kept in the dark was analysed.

As Tables 1~4 show, it may be said that the acid values and iodine values of the oils in question were not changed by heating or storing. It seems that the irregular values determined grow mainly out of the deviations of the samples. Though the acid values of olive oil and tuna oil changed slightly, we regret to say that we are not in a position to confirm this fact, for there are not many data in the present experiment.

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(2) E. Fulmer & T. C. Manchester, Jl. Amer. Chem. Soc. (1478), 1908.

(3) I. D. Messer, Paint, Oil & Chemical Review, Vol. 92, No. 24, 1931.

(4) Jl. of the Imperial Fisheries Institute, Vol. 12, No. 4, 1916.

(5) Nakao & Ikebe, Report of the Central Station of the South Manchurian Railway Company, Vol. 7, 1922, Vol. 11, 1927.

(6) Hirose, Jl. of the Soc. Chem. Ind. Japan, Vol. 28 (16), 1925.

Table I.

Acid values and iodine values of oils packed in cans and heated.

(Quantity of oil packed in a can: 170gm—There was little or on head space in the can)

	Temperature of heating C°)	Time of heating (hrs)	Acid value	Iodin value
Cotton seed oil (I)	original oil		0.04	107.1
	113	1	0.08	107.5
		1½	0.08	107.1
	116	1½	0.09	107.0
		2½	0.07	106.1
Cotton seed oil (II)	original oil		0.08	106.8
	113	1	0.08	106.8
		1½	0.06	106.7
	116.5	1½	0.07	106.6
		2½	0.06	105.6
Soya bean oil (I)	original oil		0.10	135.8
	113	1	0.16	135.7
		1½	0.10	136.0
	116.5	1½	0.15	135.5
		2½	0.13	134.8
Soya bean oil (II)	original oil		0.25	135.5
	113	1	0.20	135.9
		1½	0.17	135.8
	116.5	1½	0.19	135.4
		2½	0.14	134.6
Olive oil (I)	original oil		1.48	81.2
	113	1	1.53	81.6
		1½	1.47	81.6
	116.5	1½	1.57	81.4
		2½	1.53	80.8
Olive oil (II)	original oil		4.17	84.7
	113	1	4.37	84.8
		1½	4.35	84.7
	116.5	1½	4.38	84.8
Tuna oil	original oil		1.65	179.7
	110	1⅓	1.67	179.5
	115.2	1⅓	1.70	179.0

TABLE II.

Acid values and iodine values of cottonseed oil, soya bean oil, olive oil and tuna oil packed in cans and heated during storage.

(Oil packed in a can 170gm in weight, little or no head space in the can, and heated for 1⅓ hours)

Oil	Time of storage of canned oil (days)	Acid value			Iodine value		
		Temperature of heating (C°)			Temporature of heating (C°)		
		110	113	115.2	110	113	115.2
Cotton seed oil (I)	Original	0.14			107.4		
	72	0.13	0.15	0.17	106.5	106.7	106.8
	231	0.10	0.11	0.10	107.4	107.5	107.3
	323	0.04	0.09	0.11	107.4	107.2	106.7
	722	0.12	0.11	0.10	107.2	107.0	107.0
Cotton seed oil (II)	Original	0.10			109.2		
	99	0.11	0.08	0.06	108.4	108.6	108.7
	323	0.06	0.07	0.06	109.0	109.0	108.6
	730	0.14	0.16	0.14	108.7	108.9	109.0
Soya bean oil (I)	Original	0.18			134.8		
	101	0.23	0.20	0.18	134.5	134.4	134.0
	234	0.12	0.18	0.18	135.6	135.4	135.6
	323	0.19	0.12	0.15	135.0	135.0	134.4
	734	0.26	0.22	0.23	135.4	135.4	136.0
Soya bean oil (II)	Original	0.34			135.4		
	104	0.25		0.27	134.5		134.0
	323	0.28		0.42	135.5		135.0
	736	0.14		0.18	135.8		135.5
Olive oil (I)	Original	1.60			83.7		
	72	1.62			83.4		
	106	1.65	1.66	1.71	83.5	83.3	83.5
	236	1.66	1.57	1.74	83.7	83.7	83.8
	323	1.73	1.90	1.72	84.0	83.5	83.5
	740	1.91	1.88	1.87	83.5	83.7	83.7
Olive oil (II)	Original	1.96			86.6		
	110	1.95		1.97	86.7		86.3
	323	2.07		2.13	86.7		86.0
	736	2.31		2.31	86.8		86.8
Albacore oil	Original	1.52			179.7		
	94	1.67		1.70	179.5		179.2
	241	1.77		1.77	179.0		179.0

Table III.

Acid values of cottonseed oil, soya bean oil, olive oil and tuna oils packed in glass bottles and kept in the dark.

Time of storage (days)	Cottonseed oil		Soya bean oil		Olive oil		Albacore (Germo germo) oil				Black Tuna (Thunnas orientalis) oil	Barred Marlin (Makaira mitsukurii) oil
	(I)	(II)	(I)	(II)	(I)	(II)	(I)	(II)	(III)	(IV)		
Original	0.14	0.10	0.18	0.34	1.60	1.96	1.48	1.52	1.64	1.49	0.39	0.46
100～105	0.13	0.09	0.18	0.28	1.60	1.95	1.47	1.58	1.90	1.65	1.36	0.63
274～282	0.10	0.12	0.12	0.41	1.74	2.11	1.71	1.79	2.31	1.81	0.60	0.94
684～685	0.30	0.21	0.29	0.25	2.11	2.57	2.27	2.18	4.07	2.38	1.87	1.72

Table IV.

Iodine values of cottonseed oil, soya bean oil, olive oil and tuna oils packed in glass bottles and kept in the dark.

Time of storage (days)	Cottonseed oil		Soya bean oil		Olive oil		Albacore (Germo germo) oil				Black Tuna (Thunnas orientalis) oil	Barred Marlin (Makaira mitsukurii) oil
	(I)	(II)	(I)	(II)	(I)	(II)	(I)	(II)	(III)	(IV)		
Original	107.4	109.3	134.8	135.4	83.7	86.6	185.0	179.7	182.3	178.2	171.6	174.2
100～105	106.4	108.3	134.2	135.0	83.7	86.0	180.7	176.2	179.4	167.0	170.0	173.0
274～282	106.1	108.6	134.7	134.8	83.5	86.7	184.3	180.0	180.5	176.2	173.0	174.7
684～685	107.0	108.4	134.5	134.6	83.3	86.5	184.0	178.2	175.5	176.5	165.0	171.5

2. Experiments on mixing of oils.

The values of physical and chemical characteristics of the mixture of two oils should be determined in proportion to the mixed ratio.

The present experiments have been done for the purpose of ascertaining whether the characteristics of the mixture show actually the theoretical values or not, not only when oils were mixed, but also when heated in canned condition.

Cottonseed oil, soya bean oil, and olive oil were respectively mixed with tuna oil. The mixtures thus obtained were packed in cans and were heated at 110°C, 113°C and 115.2°C for $1\frac{1}{3}$ hours respectively, and then the acid values and iodine values of the mixtures were determined. The ratio of the two mixed oils (vegetable oil and tuna oil) was calculated by the following formula from our data of the acid values and iodine values of the mixtures.

$$x=\frac{b\sim c}{b\sim a}\times 100$$

Where a: acid value or iodine value of oil No. 1.
b: „ or „ „ No. 2.
c: „ or „ of the mixture of oil No. 1 and oil No. 2.
x: Calculated quantity (%) of oil No. 1 in the mixture.

It is clearly seen in Tables 5∼8 that when cottonseed oil, soya bean oil and olive oil were respectively mixed with tuna oil and heated after packed in cans, the differences between the calculated proportions of the mixtures (calculated from the acid values of the mixtures) and the real proportions of the mixtures were generally more than 3%, but when calculated from the iodine values, the differences were less than 1%.

Table V.

Acid values of the mixtures of vegetable oils and tuna oil.

Vegetable oil	Percentage of vegetable oil	Acid value	Percentage of vegetable oil calculated from acid value (x)	Difference between real and calculated percentages
Cottonseed oil (I)	100	0.10	—	—
	74.5	0.58	71.9	− 2.6
	49.0	0.91	52.6	+ 3.6
	25.8	1.31	29.2	+ 3.4
	0	1.81	—	—
Cottonseed oil (II)	100	0.12	—	—
	72.5	0.71	73.0	+ 0.5
	49.9	1.25	48.4	− 1.5
	23.1	2.01	13.7	− 9.4
	0	2.31	—	—
Soya bean oil	100	0.12	—	—
	77.2	0.20	83.3	+ 6.1
	48.5	0.38	45.8	− 2.7
	27.5	0.54	12.5	−15.0
	0	0.60	—	—
Olive oil	100	1.74	—	—
	76.4	1.68	92.5	+16.1
	59.5	1.30	45.0	−14.5
	33.0	1.18	30.0	− 3.0
	0	0.94	—	—

TABLE VI.

Iodine values of the mixtures of vegetable oils and tuna oil.

Vegetable oil	Percentage of vegetable oil	Iodine value	Percentage of vegetable oil calculated from iodine value (x)	Difference between real and calculated percentages
Cottonseed oil (I)	100	106.1	—	—
	71.1	126.7	70.6	−0.5
	51.2	141.5	49.5	−1.7
	35.2	152.0	34.6	−0.6
	0	176.2	—	—
Cottonseed oil (II)	100	108.6	—	—
	72.5	128.6	72.2	−0.3
	50.0	145.0	49.3	−0.7
	34.9	156.2	33.8	−1.1
	0	180.5	—	—
Soya bean oil	100	134.7	—	—
	70.0	145.5	71.8	+1.8
	45.7	154.3	48.8	+3.1
	29.7	159.6	35.0	+5.3
	0	173.0	—	—
Olive oil	100	83.5	—	—
	72.3	109.2	71.8	−0.5
	50.8	128.5	50.7	−0.1
	36.6	141.5	36.4	−0.2
	0	174.7	—	—

Table VII.

Acid values of the mixtures of cottonseed oil and tuna oil packed in cans and heated.

(Oil packed in a can 170gm in weight, little or no head space in the can.)

Temperature (C°) and time (hrs) of heating / Cottonseed oil (%)	Canned and heated									Unheated		
	110°C, 1⅓ hrs.			113°C, 1⅓ hrs.			115.2°C, 1⅓ hrs.					
	Acid valu e	x	d	Acid value	x	d	Acid value	x	d	Acid value	x	d
100	0.15	—	—	0.14	—	—	0.17	—	—	0.13	—	—
75	1.29	74.3	−0.7	1.29	74.2	−0.8	1.36	73.7	−1.3	1.29	75.4	+0.4
50	2.51	47.0	−3.0	2.46	47.2	−2.8	2.49	48.7	−1.3	2.45	50.7	+0.7
25	3.54	23.8	−1.2	3.54	24.1	−0.9	3.42	28.2	+3.2	3.68	24.6	−0.4
0	4.60	—	—	4.62	—	—	4.70	—	—	4.84	—	—

x: Percentage of cottonseed oil calculated from acid value.
d: Difference between real and calculated percentages.

Table VIII.

Iodine values of the mixtures of cottonseed oil and tuna oil packed in cans and heated.

(Oils packed in a can 170gm in weight, little or no head space in the can.)

Temperature (C°) and time (hrs) of heating / Cottonseed oil (%)	Canned and heated									Unheated		
	110°C, 1⅓ hrs.			113°C, 1⅓ hrs.			115.2°C, 1⅓ hrs.					
	Iodine value	x	d	Iodine value	x	d	Iodine value	x	d	Iodine value	x	d
100	106.6	—	—	106.5	—	—	106.7	—	—	106.5	—	—
75	130.0	74.0	−1.0	129.7	74.3	−0.7	129.3	72.8	−2.2	129.0	74.8	−0.2
50	152.0	49.5	−0.5	151.6	50.0	0	151.5	49.0	−1.0	151.6	49.6	−0.4
25	174.5	24.5	−0.5	173.4	25.7	+0.7	173.5	25.3	+0.3	173.0	25.7	+0.7
0	196.5	—	—	196.6	—	—	197.0	—	—	196.0	—	—

x: Percentage of cottonseed oil calculated from iodnie value.
d: Diffcrence between real and calculated percentages.

(II) Acid values and iodine values of oils in canned tuna in oils.

The experiments on oils were carried out as above, then tuna was packed in cans respectively with several vegetable oils, and then the oils in the canned tuna were analysed while they were kept intact.

Refrigerated albacore (Germo germo) was melted in the air and heated by the steam for three hours in a retort, and left at room temperature for twenty-four hours. The white part of flesh thus obtained was so fully packed in cans together with each vegetable oil as to leave little or no head space in the cans. The contents of one can were as the following. Tuna flesh 170 gm, NaCl 4.5 gm, vegetable oil 30 gm.

The canned tuna in oils were sterilized by heating at 110°C, 113°C and 115.2°C for $1\frac{1}{3}$ hours respectively in the retort.

Canned tuna in oil being opened and kept leaning to one side for twenty minutes, oil and juice in the can were pourred out. The mixture of oil and juice was heated on the water bath for thirty minutes, and the oil was separated from the juice, then the acid value and iodine value of the oil were determined.

As Table IX shows the acid values and iodine values of oils did not change though they were heated on the water bath for thirty minutes.

As given in tables X and XI the acid values of the oils (outside of the albacore flesh in the can) in canned albacore in oils or in water showed the increasing tendency during the storage of the cans for 700 days, but no regular change was observed in the iodine values.

From the fact that there was little or no change in the iodine values, it may be presumed that there was no change in the constitution of the oils in the cans, and therefore the mixed ratio of tuna oil and the vegetable oil added may be calculated from the iodine values.

As Table XII shows, the calculated quantities of the vegetable oils were about 75%.

The calculated acid values (calculated from the mixed ratios of tuna oil and vegetable oils and the figures in Table II and Table XI) are less than the determined values, and the difference between those twe after the storage of the cans for 700 days is greater than that at the beginning of the storage.

It is very interesting to know whether the increasing tendency of the acid values takes its origin from the oxidation of the oils in the cans or not. This question should be studied in future.

Table IX.

Acid values and iodine values of the oils mingled with the juice from canned tuna and heated on the water bath.

(Canned tuna was sterilized by heating at 115.2°C for 1⅓ hours. Oils were packed in cans and heated at 115.2°C for 1⅓ hours. Proportion of the mixture—oil 15 c.c. : juice 5 c.c.)

Time of heating on the water bath. (minutes)	Acid value			Iodine value		
	Cottonseed oil	mixture of cottonseed oil and tuna oil (50%+50%)	Tuna oil	Cottonseed oil	mixture of cottonseed oil and tuna oil (50%+50%)	Tuna oil
Original (unheated)	0.03	2.42	5.26	106.6	150.4	194.0
30	0.05	2.41	5.13	106.5	150.4	194.2
60	0.04	2.48	5.09	106.4	150.5	192.8
120	0.05	2.47	5.15	106.6	149.9	193.0

Table X.

Acid values and iodine values of the oils found outside of the flesh in canned albacore in vegetable oils.

(Contents of a can : Albacore flesh 170^{gm}, NaCl 4.5^{gm}, vegetable oil 30^{gm}—There was little or no head space in the can. Time of heating : 1⅓ hours.)

Vegetable oil	Time of storage of canned albacore in oil (days)	Acid value			Iodine value		
		Temperature of heating (C°)			Temperature of heating (C°)		
		110	113	115.2	110	113	115.2
Cottonseed oil (I) (Acid value 0.14 Iodine value 107.4)	92	0.71	0.60	0.82	129.3	124.1	127.2
	232	0.82	0.67	0.72	133.3	128.0	126.4
	324	0.75	0.93	0.70	119.3	125.8	120.9
	729	1.24	1.17	1.03	120.8	127.2	125.0
Cottonseed oil (II) (Acid value 0.10 Iodine value 109.2)	98	0.71	0.79	0.51	126.5	126.8	116.8
	328	0.96	0.72	0.82	128.0	127.8	123.0
	733	1.62	1.50	0.80	131.5	131.4	120.0

Vegetable oil	Time of storage of canned albacore in oil (days)	Acid value			Iodine value		
		Temperature of heating (C°)			Temperature of heating (C°)		
		110	113	115.2	110	113	115.2
Soya bean oil (I) (Acid value 0.18 Iodine value 134.8)	100	0.79	0.60	0.84	144.2	144.0	145.3
	237	0.85	0.82	0.77	145.0	149.5	147.5
	330	0.93	0.96	0.84	145.4	146.3	147.3
	735	1.50	1.66	1.10	149.3	148.8	142.8
Soya bean oil (II) (Acid value 0.34 Iodine value 135.4)	105	0.92	0.60	0.67	146.0	143.5	147.5
	331	1.08	0.73	0.65	146.0	145.0	140.0
	737	1.57	0.93	1.47	151.6	149.0	151.5
Olive oil (I) (Acid value 1.60 Iodine value 83.7)	107	1.95	1.96	1.77	108.5	100.4	108.8
	239	2.01	1.77	1.93	114.0	111.5	96.0
	334	1.98	1.82	2.10	113.5	113.0	93.3
	743	2.59	2.32	2.42	116.0	100.3	113.3
Olive oil (II) (Acid value 1.96 Iodine value 86.6)	111	2.16	1.73	1.94	110.0	109.5	105.0
	335	2.42	2.08	2.29	108.0	110.0	105.5
	748	2.83	2.45	2.82	107.4	107.6	106.0

TABLE XI.

Acid values and iodine valves of the oils found outside of the flesh in canned albacore.

(Contents of a can : Albacore flesh 170gm, NaCl 4.5gm, water 30gm—There was little or no head space in the can. Time of heating : 1⅓ hours.)

Temperature of heating (C°) / Time of storage of canned albacore (days)	Acid value			Iodine value		
	110	113	115.2	110	113	115.2
236	1.38	—	—	186.5	—	—
336	1.46	2.29	—	181.5	—	175.5
750	3.03	2.54	3.00	184.5	175.5	178.7

TABLE XII.

Determined acid values of the oils found outside of the flesh in canned albacore in vegetable oils and calculated acid values from the proportions based on iodine values of the mixtures of vegetable oils and tuna oil.

(Average values obtained by heating at 110°C, 113°C and 115.2°C)

Vegetable oil	Time of storage of canned albacore in oil (days)	Iodine value (average)	Vegetable oil calculated from iodine value (%)	Acid value		
				Determined	Calculated	Difference
Cottonseed oil (I)	92	125.6	74.7	0.71	0.46	0.25
	232			0.74	0.42	0.32
	324			0.79	0.53	0.26
	729			1.15	0.80	0.35
Cottonseed oil (II)	98	125.7	76.3	0.67	0.39	0.28
	328			0.83	0.49	0.34
	733			1.31	0.80	0.51
Soya bean oil (I)	100	146.3	75.2	0.74	0.49	0.25
	237			0.81	0.46	0.35
	330			0.91	0.58	0.33
	735			1.42	0.89	0.53
Soya bean oil (II)	105	146.7	74.3	0.73	0.55	0.18
	331			0.82	0.74	0.08
	737			1.32	0.85	0.47
Olive oil (I)	107	107.4	75.5	1.89	1.60	0.29
	239			1.90	1.59	0.31
	334			1.97	1.80	0.17
	743			2.44	2.13	0.31
Olive oil (II)	111	107.7	77.0	1.94	1.83	0.11
	335			2.26	2.05	0.21
	748			2.70	2.44	0.26

Summary

1. The authors carried out the following experiments with respect to the ripeness of canned tuna in oil.

(a) Chemical studies on heating, storing and mixing of oils.

(b) Determination of acid values and iodine values of oils in canned tuna in oils.

2. (a) When cottonseed oil, soya bean oil, olive oil and tuna oil were respectively packed in cans fully—there was little or no head space in the can—and heated at 116.5°C for $2\frac{1}{2}$ hours, (b) when these oils were heated at 110°C, 113°C and 115.2°C for $1\frac{1}{3}$ hours respectively after canned and were kept intact for 700 days, it is not wrong to say that the acid values and iodine values did not change, but in olive oil and tuna oil the changeable tendency of acid values was observed.

3. When cottonseed oil, soya bean oil and olive oil were respectively mixed with tuna oil and were heated after packed in cans, the iodine values of the mixtures were determined in proportion to the mixed ratio.

4. The acid values of the oils found outside of the albacore flesh in canned albacore in cottonseed oil, soya bean oil and olive oil showed the increasing tendency during the stotage of the cans for 700 days, but no regular change of the iodine values was observed.

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Experimental Studies of the Water Movement in Coastal Regions of the Sea. I. Tidal Oscillations in Sagami Bay.

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Introduction.

In carrying an experimental study of water movements in a bay or a strait, one is encountered by difficulties which interfere with reproduction on a reduced scale of various actual conditions, especially those of forces acting on the mass of water, such as the deflecting force of earth's rotation and the tide producing forces. Moreover, the general quantitative relation between the actual water movements and the reproduced ones has not yet been established, even when the effects of difference in the action of forces are put out of the question.(1) It is, therefore, desired to know in what extent and under what condition we can utilize the results of experiment for the estimation of the actual movements. The improvement of the method to be used in the experiments must, on the other hand, have solid foundation.

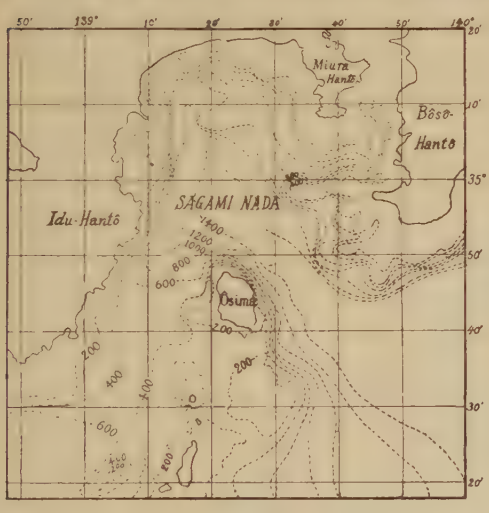


Fig. 1.

Bathymetric chart of Sagami Bay, drawn after the chart No. 80. Hydrographic Department Imperial Japanese-Navy.

Sagami Bay is situated south to Kanagawa Prefecture, and between Bôsô Peninsula on the east side and Idu Peninsula on the west. The configuration of its basin is, as shown in Fig. 1, considerably complicated. At

(1) For simple cases, the relation was studied by S. Takaya; Umi to Sora, 8 (5), 1928, 70 (in Japanese).

about the midway of the mouth, Sagami Bay has a large island called Ôsima. The maximum depth of the mouth of the bay is over 1,800 meters on the east side of Ôsima, while it is less than 500 meters on the opposite. To the south and southwest of Ôsima there lies the crest of the ridge running S 10°E across the western North Pacific which seems to have much influences on the water movement in this bay. Few direct observations of the latter, however, have hitherto been carried out, except on a few spots[1] near the coast, while the results of chemical and thermometrical observations have

Fig. 2.

The plan of the model, with apparatus to set the water in oscillation. Dotted lines show the isobaths; *a*, *b*, *c*,.....*h*, *A*, *B* and *C*: the position at which the wave was observed; *C'*: the canal; *E'*: the piston, and *F'*: the vertical cylinder.

(1) Some results of current observations are given in recent numbers of Semi-anual Report of Oceanographical Investigation published by the Imperial Fisheries Experimental Station, Tokyo.

revealed the existence of a marked stratification of several kinds of water of different origins flowing in this bay. The stratification will also affect the mode of the water movement.

In the present paper a method of experimental studies of the periodic oscillation of water modeled after the semidiurnal tidal motion in Sagami Bay and its vicinity is described. Some qualitative results are also given.

Apparatus used in the experiments.

The model of the basin of the sea in the region as shown in Fig. 2 was made of cemented bricks in a large rectangular wooden tank, 2.55 m × 2.60 m wide and 0.42 m high. The scale of linear dimension was so chosen that 125 cm correspond to 100 km for horizontal distances, while 1.75 cm correspond to 100 m for the vertical depths. Fig. 2 shows the isobaths in the model and Fig. 1 those obtained from the chart No. 80 published by the Hydrographic Department of the Imperial Japanese Navy in 1930.(1) The surface of the bricks was coated with cement. In the experiments to be reported below the region having the depth of over 1,000 m was filled with fine gravels up to the same depth. Passing through the point at about 118 km to the south of Ôsima a straight barrier, made of wooden plank, was supported vertically in water in the direction of N 60°E, so that the water was forced to move in the same direction along the line of the barrier. The direction of the barrier was determined to be perpendicular to the co-tidal line of M_2 tide given in a chart made by Dr. S. Ogura.(2) Plate I shows the general view of the apparatus.

To set the water in oscillation a rectangular canal C was made on the outside of the barrier B and a wooden plate E, just fit the cross-section of the canal, was made to move back and forth by the aid of a piston-rod to which the plate was fixed at its top. The piston was connected to a crank disc D with a connecting rod movable about the crank-pin screwed on the surface of the crank disc at a suitable distance from the centre of the disc. The crank shaft was driven with an exchangeable gear and a worm on the shaft of a

(1) At the beginning of the experiments in 1930, the chart based on the results of new soundings had not yet been published, and the depths in the model differ considerably from the corresponding actual ones.

(2) Recently Dr. Ogura has published a new chart of co-tidal lines of M_2 in the vicinity of Japan, in which the direction of the co-tidal lines at the position of the barrier is altered to N 10°W.—S. Ogura: The Tides in the Seas Adjacent to Japan. Bull. Hydrogr. Departm. Imper. Japan. Navy, Vol. VII, 1933.

motor *M*. The range and period of the stroke of piston were thus made to be adjustable. Each end of the canal led to each side of the model, *i. e.* to the south of Idu or Bôsô Peninsula, through the teeth of a set of vertically supported zinc sheets curved in a form of stream lines, and fixed at the bottom of the tank, as shown in Fig. 2 and Plate I. The oscillation of water in the model became stationary about half an hour after the piston had been set into motion.

In some experiments, where it was required to modify the phase of the tides in relation to that of tidal currents, a circular cylinder, 15 cm in diameter, was suspended in the canal with steel wire connected to the crank pin on the crank disc. The wire was lapped on the pulleys situated at suitable position over the canal. Thus we obtained any phase-difference according to the angle between the wire and the piston-rod, subtended at the centre of the crank disc.

Stratification of the water and the rotation of the earth were not realized.

Methods of observation and measurements.

Records were taken chiefly of the currents at, and vertical oscillations of, the surface of water. The current beneath the surface was also measured at a depth of 400 m in a few cases.

To observe the surface currents, alminium powder was scattered on the surface and the paths of particles of powder were photographed from above by the 3 minutes' exposure commencing at the end of every 12th division of the period of oscillation. The water was tinted with potassium permanganate lest the image of the bottom should not have been printed on the photographic plate, having obscured the paths of the powder. No particular illumination was made use of.

To record the elevation and depression of the surface a special apparatus was used. Fig. 3. shows the apparatus. The principle on which the function of this apparatus is based is an application of a torsion balance, the lever of which is connected to an horizontal ring pulled down by the action of surface tension of the water. When the ring is just placed on the surface and the lever is balanced with some counterweights, the ring follows in detail the vertical motion of the surface, the lever rotating up and down about the stretched wire of the torsion balance. The rotation of the lever was recorded, using optical levers, on a photographic plate in a falling plate-camera. The ring used was made of galvanized iron wire, 0.9 mm in diameter, bent in a

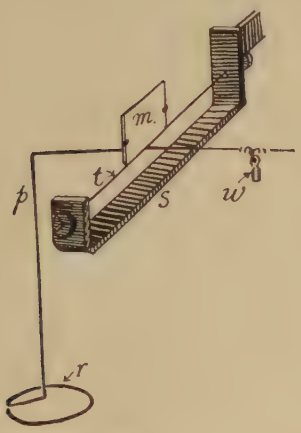


Fig. 3.

Instrument used to record the tidal motion of the surface.

r: the ring put on the surface of water.
t: stretched wire.
m: mirror.
w: counterweight.

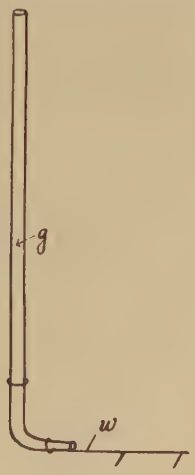


Fig. 4.

Instrument used to measure the current beneath the surface.

g: glass tube containing potassium permanganate.
w: horizontal wire having two marks 2cm apart.

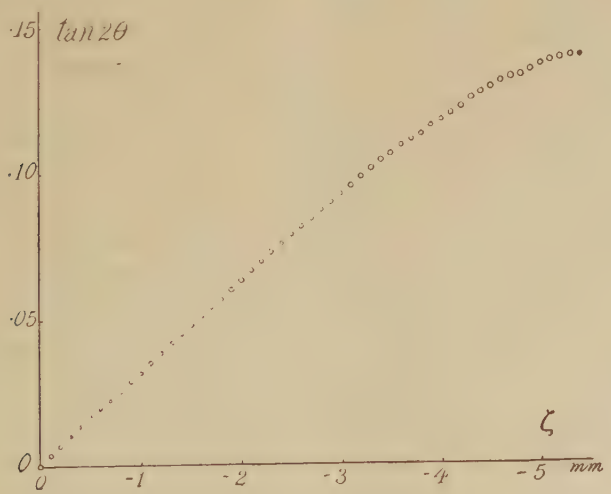


Fig. 5.

An example showing the result of calibration of the tide-recording instrument.
ζ: the elevation of the water surface, θ: the angle of rotation of the mirror.

circle having radius of 7.7 mm. A result of calibration of the apparatus is given in Fig. 5. The constant of proportion between the angle of rotation of the torsion balance and the elevation of the water surface varies slightly according to the position of the lever. In the experiments, however, the elevation of the surface did not exceed 1 mm, while the length of the optical lever exceeded at least 1.5 meters, and therefore we can assume the proportionality between the elevation of the water surface and the displacement of the records on the photographic plate. On the other hand, the constant of proportion must depend on the neutral position of the ring relative to the undisturbed water surface, on the weight and position of the counterweight, on the tension of the stretched wire, &c. All such conditions were, during the experiments carried out in darkness, practically impossible to be examined in each case. Therefore the range of vertical oscillations was measured separately in day-time with a micrometer-microscope, aiming at the shadow cast by a pin vertically supported above the surface at the same position where the record of the wave was taken at night.

In order to record the motion of the piston-rod simultaneously with the wave on the plate, two bundles of parallel beams were sent through two parallel slits to the mirror fixed on the lever of torsion balance and one of the slits was made to close automatically when the keys, situated at the piston-rod, made an electric circuit of a battery. Several of such keys were arranged successively at different distances from each preceding one, and we can decipher the position of the piston-rod, at any instant, from the different stripes superposed on the curve as shown in Plate II. The period of oscillation was measured in beforehand with a stop-watch, and on the photographic plates too, a series of dots were printed by sending the flashes of a lamp through a pin-hole to the camera, at every instant when a pendulum made a circuit of the lamp.

The current beneath the surface was measured only at several points. A fine glass tube, whose lower end was bent at right angles as shown in Fig. 4, were supported vertically in water from above. A drop of water coloured with potassium permanganate was let go out into water through the glass tube put at a desired depth, when the motion of the piston attained the maximum velocity on the midway of both its journeys back and forth. The direction was observed from above and sketched. Then the end of the tube was set in this direction. At the next time, when the piston came again the same position as before, a drop of coloured water was let go out from the end of the tube along a fine wire fixed to the end of the glass tube as shown in

Fig. 4. The time taken for the colour to pass 2 cm between two marks on the wire was measured with a stop-watch in hand, the speed of the flow having been calculated afterwards.

Experiments carried out.

In the present experiments, the period, T, of the oscillations was exclusively about 50 seconds. Considerable fluctuations of the speed of motor could not be eliminated, resulting the variation of about 5% in the magnitude of T. The range of stroke of the piston was 22 cm. Two series of experiments were carried out.

In the first experiement only the piston was used to move the water, while in the second, the motion of the vertical cylinder was made to joint to that of the piston. The angle made at the disc between the wire suspending the cylinder and the piston-rod was 67.5°. The piston came to its eastern end position after the disc rotates by 67.5° starting from the instant at which the cylinder sunk to its deepest position. The stroke of the vertical motion of the cylinder ranged 21.5 cm.

The results of experiments.

Plate II shows the record of wave motion of the surface obtained in the first experiment at the three points A, B and C on the outside of the Sagami Bay, as are shown in Fig. 2, while Plate III shows the same thing obtained in the second experiment. Glancing at these curves, it is evident that in the first experiment, the wave is a standing one, having a nodal line passing between the two points B and C in Fig. 2, while in the second experiment, the wave is progressive, propagating from east to west. The results of harmonic analysis of the curves in Plate III show that the mean velocity of propagation of the first harmonic wave is about 16 cm/sec, if we assume that the direction of propagation of the wave is S 62°W, the difference in phase of the waves at A and C being 36°. The other records, obtained in the interior of Sagami Bay, indicate the existence of a slight phase-difference among them. Fig. 6 shows the values at the points a, b, c, d, e, f, g, h and k as well as at A, B and C, shown in Fig. 2, of η in the expression $H = H_0 \cos\left(2\pi \frac{t}{T} - \eta\right)$, where H denotes the first harmonic of each wave, T the period, t the time measured from the instant at which the piston-rod is at

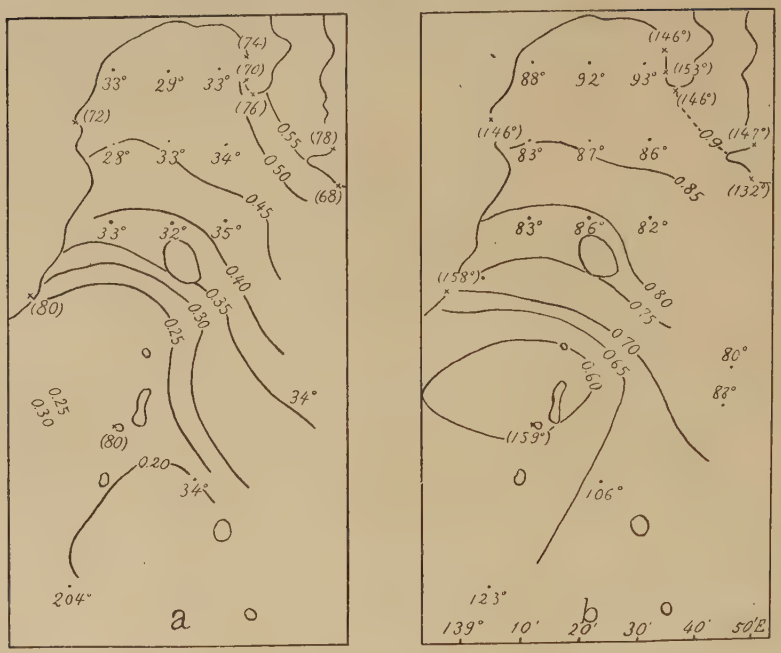


Fig. 6.

Maximum tidal range in mm (thick lines), and phase of tidal wave observed in the first (a) and the second (b) experiments. Bracketed numerals give $2H$ cm (in a) and k (in b) of M_2 tide.

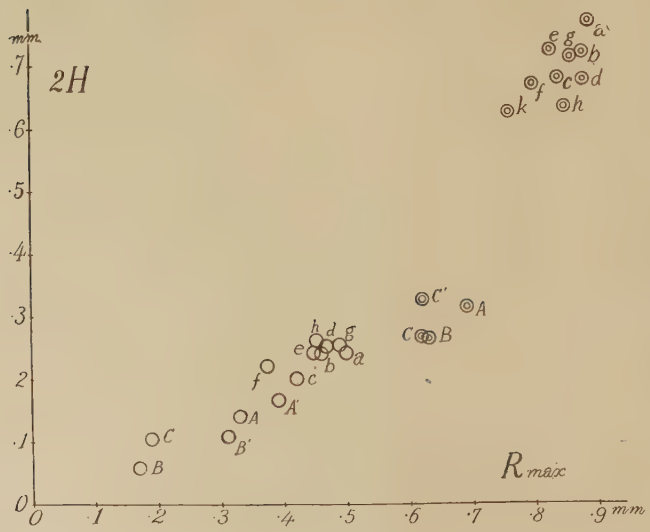


Fig. 7.

The range of the first harmonic wave $2H$ in relation to the maximum tidal range R max. observed in the first ○ and the second ◎ experiments.

its western end position. In the case of second experiment, the wave proceeds toward the north in general in a complicated way.

Fig. 6 shows also the values of maximum range of vertical oscillations observed with a microscope, as mentioned above. These values include the effects of disturbances, such as capillary waves and the secondary undulations. Comparison with the photographic records of waves at the twelve points shows that this maximum range varies with the values of $2H$, the range of the first harmonic, as shown in Fig. 7. It is remarkable that the values of maximum range in the first experiment is everywhere less than that in the second experiment by a constant amount, about 0.4 mm. Generally to say, the range is great along the north-eastern coast of Sagami Bay. It diminishes towards southwest.

The Plates IV~XV give the records of surface currents. The number, $i(=1, 2, \ldots\ldots 12)$ on the cards at the top of each photograph shows the time, $(i-1)\,\frac{T}{12}$, of commencement of the exposure relative to the motion of the piston, $i=1$ meaning the moment at which the piston-rod is at its western end

Table I.

v: velocity im cm/sec; α: direction measured *contra solem* from north; θ: phase relative to the motion of the piston, measured from the instant when the piston is at the western terminal. e: the sense of rotation of the ellipse of tidal current. $+$means rotation *contra solem*. Suffixes denote the number of experiment.

Points	Maximum current						Minimum current				Residual current			
	v_1	v_2	α_1	α_2	θ_1	θ_2	v_1	v_2	e_1	e_2	v_1	v_2	α_1	α_2
a	0.10	0.08	115°	95°	83°	77°	0.02	0.00	—	+	0.02	0.01	270°	333°
b	0.41	0.33	127	124	76	72	0.02	0.06	+	—	0.14	0.15	199	209
c	0.53	0.49	139	137	84	73	0.03	0.10	+	—	0.11	0.15	143	136
d	0.14	0.18	134	122	81	91	0.00	0.04	+	—	0.01	0.01	259	285
e	0.33	0.35	144	152	75	74	0.10	0.06	+	—	0.06	0.16	201	250
f	1.27	1.01	112	117	76	72	0.09	0.25	+	—	0.11	0.14	212	214
g	0.20	0.19	135	155	80	82	0.00	0.00	+	+	0.00	0.04	—	168
h	0.38	0.48	163	170	66	96	0.07	0.05	+	—	0.11	0.21	20	343
k	0.96	0.49	151	112	81	100	0.14	0.16	+	—	0.05	0.25	352	317

position. Suffix p means that the records were obtained in the second experiment. The direction of the flow is indicated by arrows. At a glance, we know that the mode of surface currents is utterly similar in the two experiments. To examine the degree of similarity in detail, the northward and the eastward components of the paths of aluminium powder were read off at the nine points a to h in Fig. 2, placing the negative plates on a millimeter paper. Harmonic analysis was applied to these components and the direction of maximum flow, the maximum and minimum velocities, and the phase referred to the instant at which the piston-rod passes its western end position,

Fig.

Currents in the second experiment, at the instants one fourth of the period after

between the two regions where the stream lines on the surface are endless or

were calculated. The results are given in Table I. It is remarkable that the direction and the speed of maximum currents as well as its phase relative to the piston-motion, are nearly the same in both of the experiments, while the hodographs of current vectors rotate mostly in opposite direction in the two experiments. In Table I the rotation *cum sole* is represented with negative sign.

The results of harmonic analysis show further the existence at several spots a non-periodic residual current of considerable speed, the direction and the speed of which are also given in Table I. This fact seems to raise an

8.

the piston has passed both terminal positions. Chain-lines show the boundary not. Surface currents are obtained from the records in Pl. VI and XII.

interesting problem seeing from the theoretical point of view.[1]

Another remarkable feature shown in the plates is that some of the stream lines have their end at the north eastern coast of Sagami Bay. The boundary line which separates two regions, where the stream lines are endless or not, is different in its form and its location for the ebb and flood currents as shown with chain-lines in Fig. 8. This fact may, when compared with the distribution of the range of tidal motion of the surface, be explained mostly by the reflection of waves, which takes place along the northern coasts of Sagami Bay.

The results of observation of currents at 400 m (7 cm) are shown in Fig. 8, together with the surface flow at the same instant (Plate VI and XII). They were obtained in the second experiment. Both ebb and flood currents follow mostly the trend of isobaths excepting the flood current at the northern margin of the bay, where the existence of vertical currents is evident.

The comparison with the actual tides and tidal currents.

There are but a few data utilizable for the comparison of the results of experiment with the actual semidiurnal components of tides and tidal currents. At present, we take all the data from the recent work of Dr. S. Ogura on "the tides in the seas adjacent to Japan" (1933), published by the Hydrographic Department of the Imperial Japanese Navy.[2] (1) The range $2H$, (2) the phase k, refered to the moon's culmination at each stations, of M_2 tide and (3) the direction and the order of magnitude of speed of the maximum flood currents are given in Figs. 6a, 6b and 8 respectively. Qualitative features of distribution of various elements of tides and tidal currents agree with those in the second experiment, except the large values of H on the outside of the western mouth of Sagami Bay.

Discussions.

The fact, that the modes of horizontal oscillations at the surface in the two experiments do not much differ from each other throughout the whole period, and indeed the very arrangement of small vortices are nearly the same, irrespective of a considerable differences in the range and the phase of vertical

(1) Cf. H. Hertz; Verhandl. d. phys. G.sel. zu Berlin, 5. Jan. 1883.
(2) Loc. cit.

wave motion, seems to suggest us an important nature of the oscillations of water in models of this kind. The attachment of the vertical motion of a cylinder to the horizontal one of the piston, as done in the second experiment, seems to have but a little influence on the horizontal movement of water, while it changes considerably, and indeed to a certain extent arbitrarily, the range and the phase of vertical oscillation of the surface.

As for the numerical relations of various elements, the results of the present experiments show that the water movements in the model were never in all respects similar to those in the actual sea, especially in respect of the difference in phase of waves at various spots, the difference in phase of waves and currents, etc.

The simplest way to obtain the provisional law for numerical comparison is to start from the equations of almost horizontal small oscillations of an incompressible non-viscous and homogeneous fluid:

$$\frac{\partial}{\partial t}(u,\ v)=-g\left(\frac{\partial}{\partial x},\ \frac{\partial}{\partial y}\right)\zeta, \qquad \frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}+\frac{\partial w}{\partial z}=0, \ldots\ldots\ (1)$$

with boundary conditions:

$$(w)_{z=0}=-\frac{\partial \zeta}{\partial t}, \qquad \left(u\frac{\partial z}{\partial x}+v\frac{\partial z}{\partial y}-w\right)_{z=z}=0, \ldots\ldots\ (2)$$

where (u, v, w) is the velocity at time t at the point (x, y, z), the axis of z being taken vertically downwards from the surface $z=0$ to the bottom $z=z$; ζ the elevation of the surface and g the acceleration due to gravity. The conditions of similitude obtained from (1) and (2) are:

$$\frac{V}{T}=\frac{Z}{L},\ \frac{W}{V}=\frac{H}{L},\ \text{and}\ W=\frac{Z}{T},$$

where V, W; L, H; T and Z are the ratios of the scale of horizontal and vertical velocities; of horizontal and vertical distances; of the time and of the elevation of surface. These conditions lead to

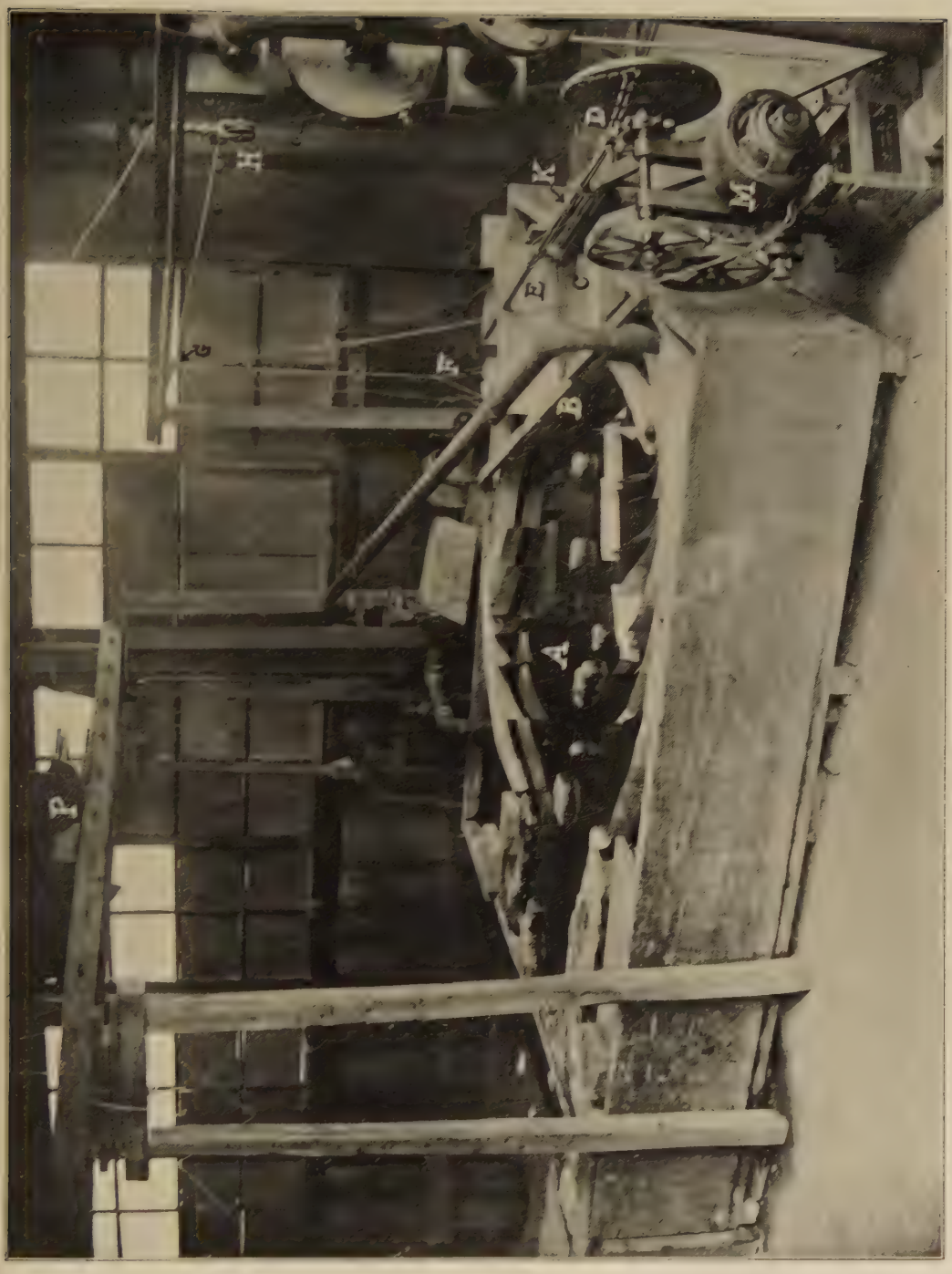
$$Z=H,\ T=\frac{L}{\sqrt{H}},\ V=\sqrt{H},\ \text{and}\ W=\frac{\sqrt{H^3}}{L}.$$

In the present experiment, $H=1.75\times10^{-4}$ and $L=1.25\times10^{-5}$. Hence $Z=1.75\times10^{-4}$, $T=9.47\times10^{-4}$ and $V=1.32\times10^{-2}$. The tidal range of 70 cm corresponds to 1.2×10^{-2} cm, the period of M_2 tide of 12.42 hours to 42.3 sec.

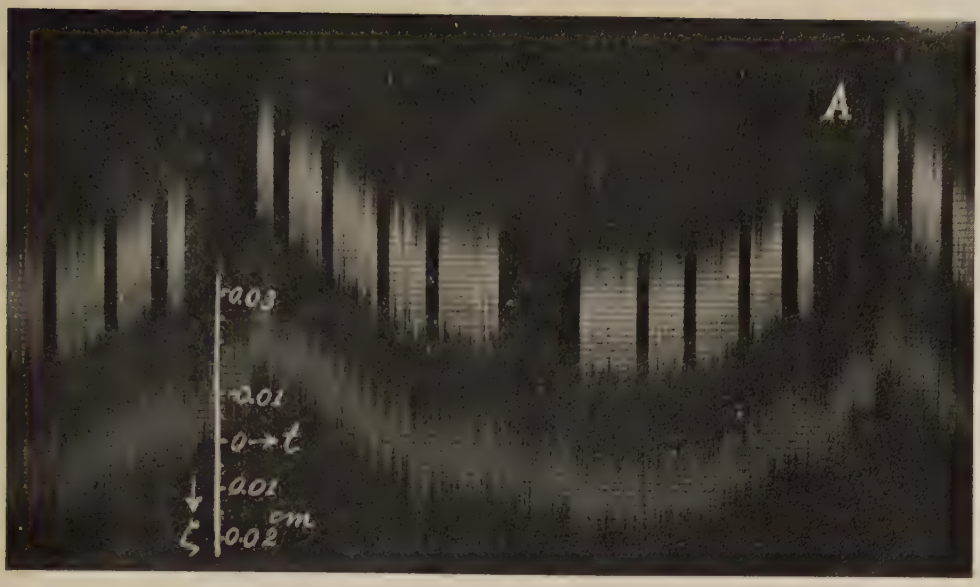
and horizontal current of 1 knot to 0.68 cm/sec. Z and T in the experiment were greater than those required from the law given above.

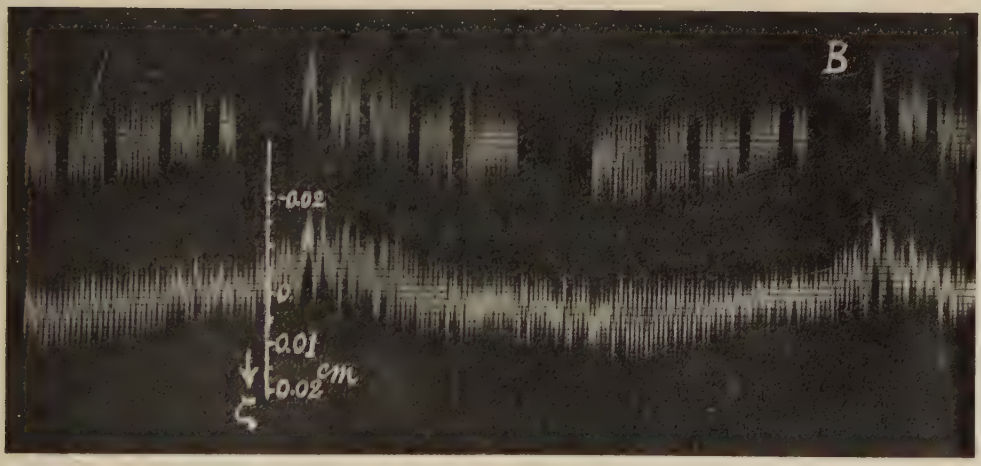
In conclusion the writers wish to express their best thanks to Dr. M. Tauti for the constant guidances and also to Mr. K. Tomimasu, Mr. M. Uda and other members of the Hydrographic Laboratory of the Imperial Fisheries Experimental Station for valuable advices rendered to them.

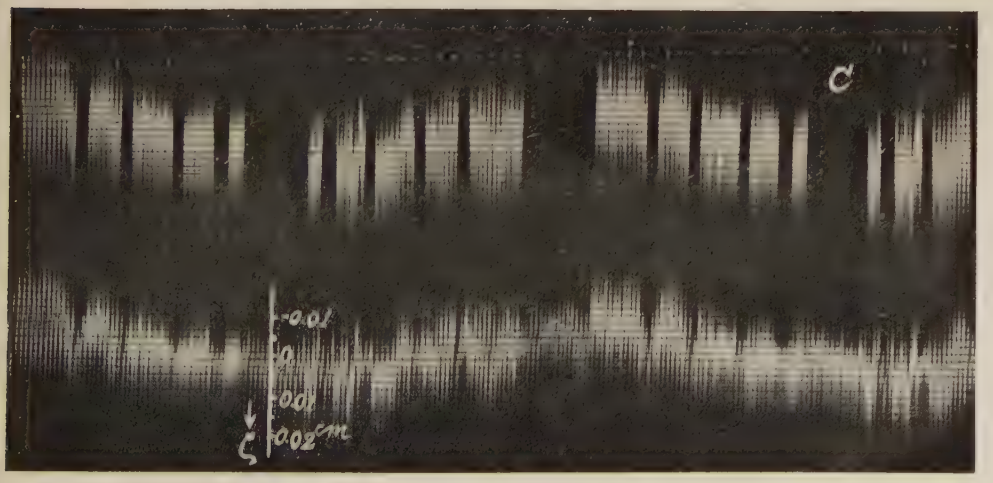
Pl. I.



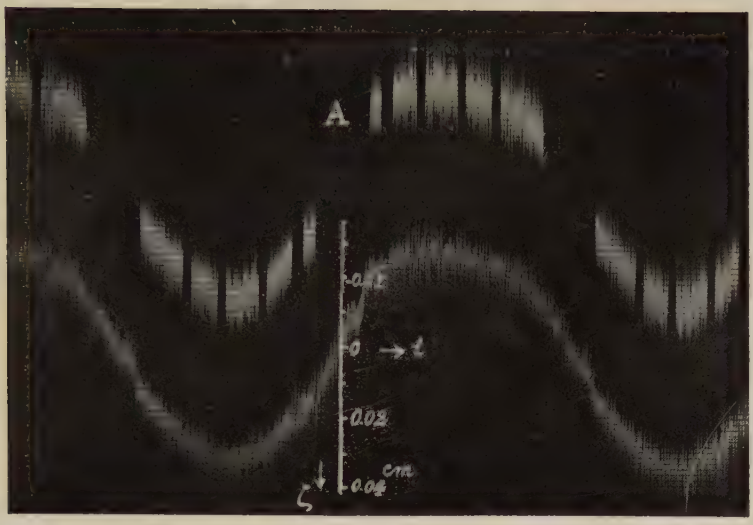
Pl. II.

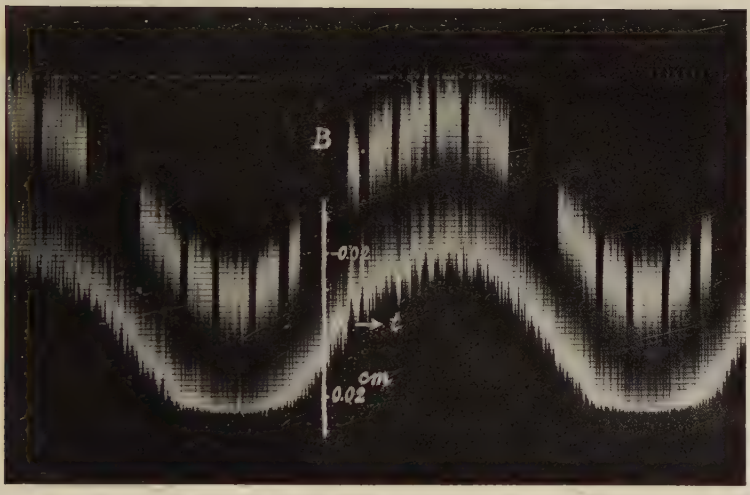


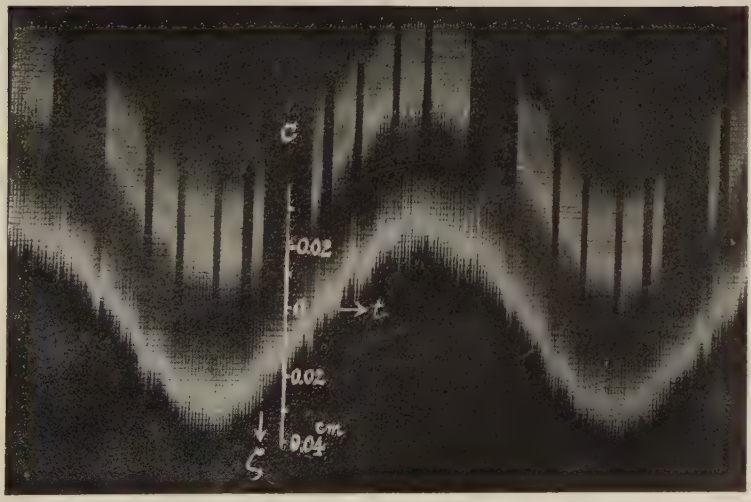




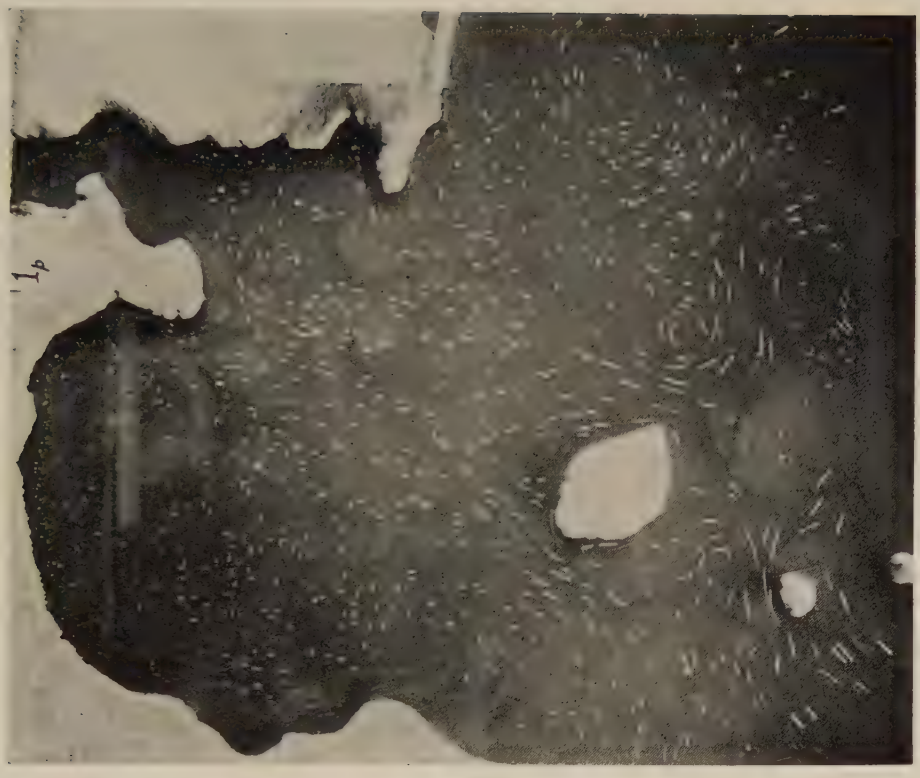
Pl. III.

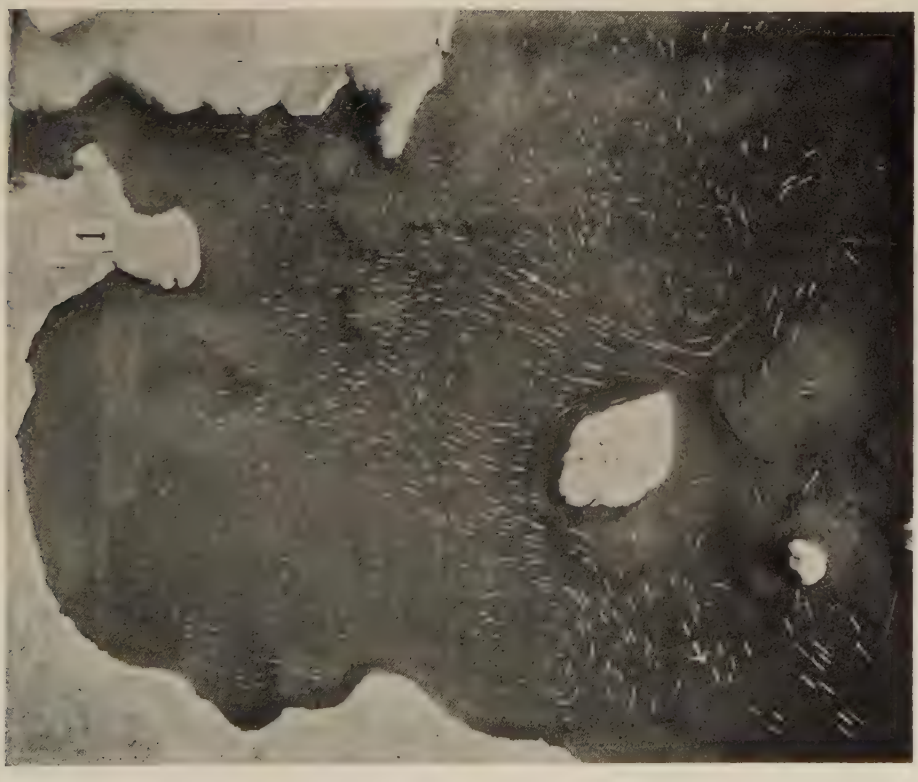




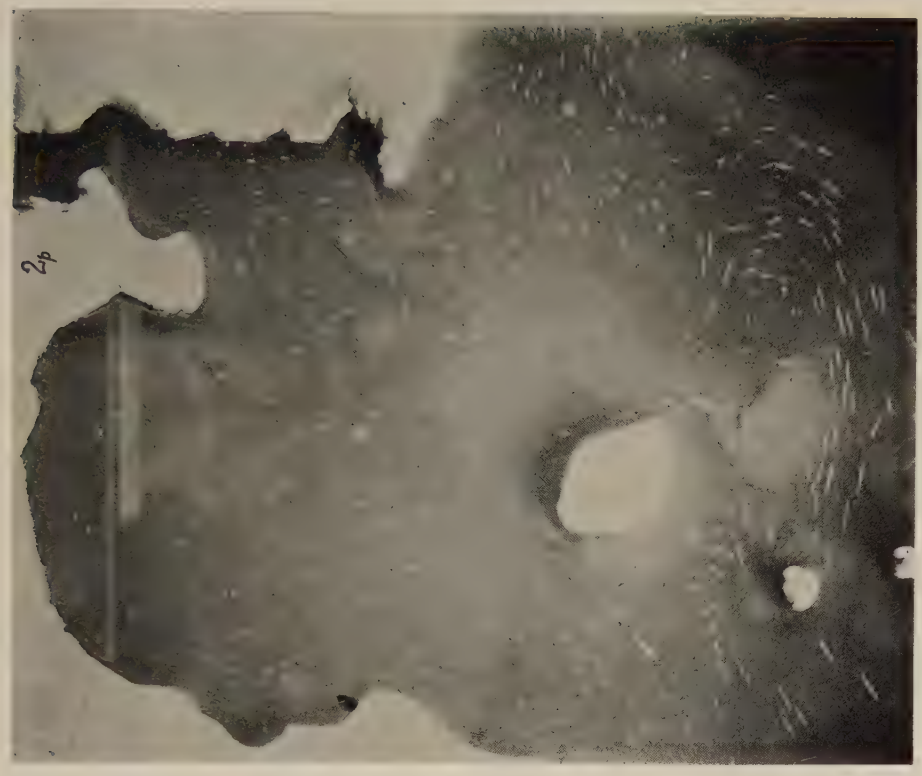


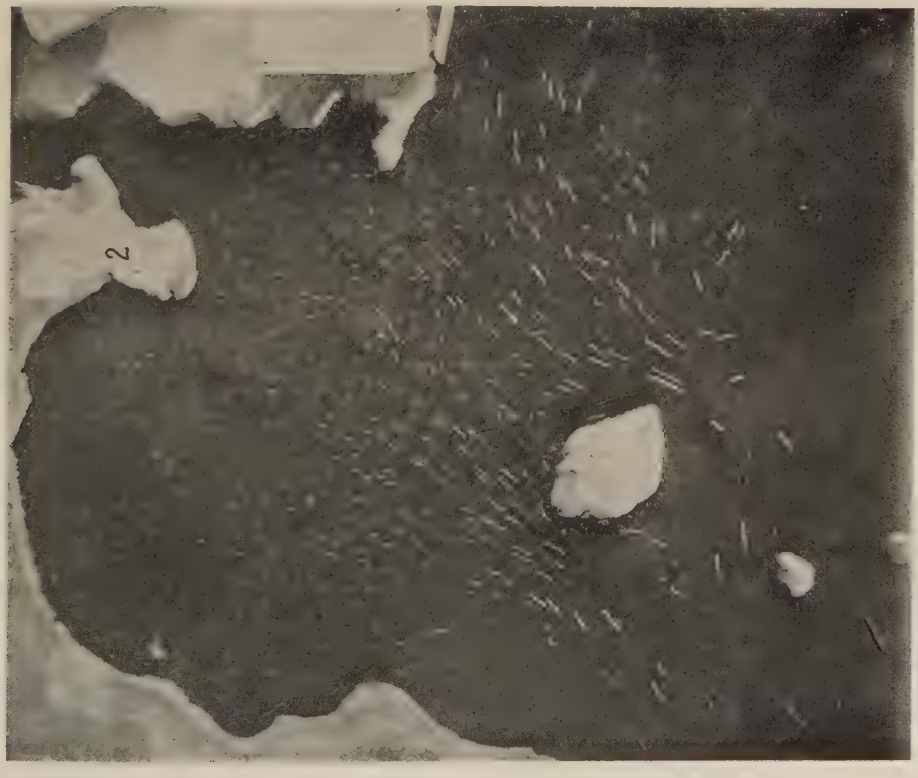
Pl. IV.



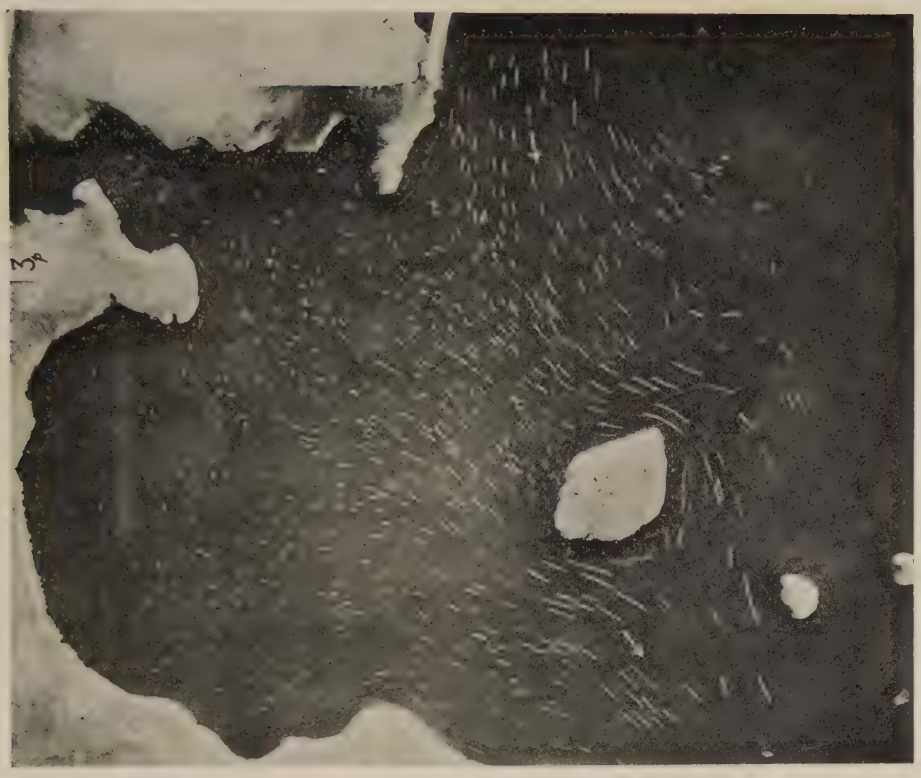


Pl. V.

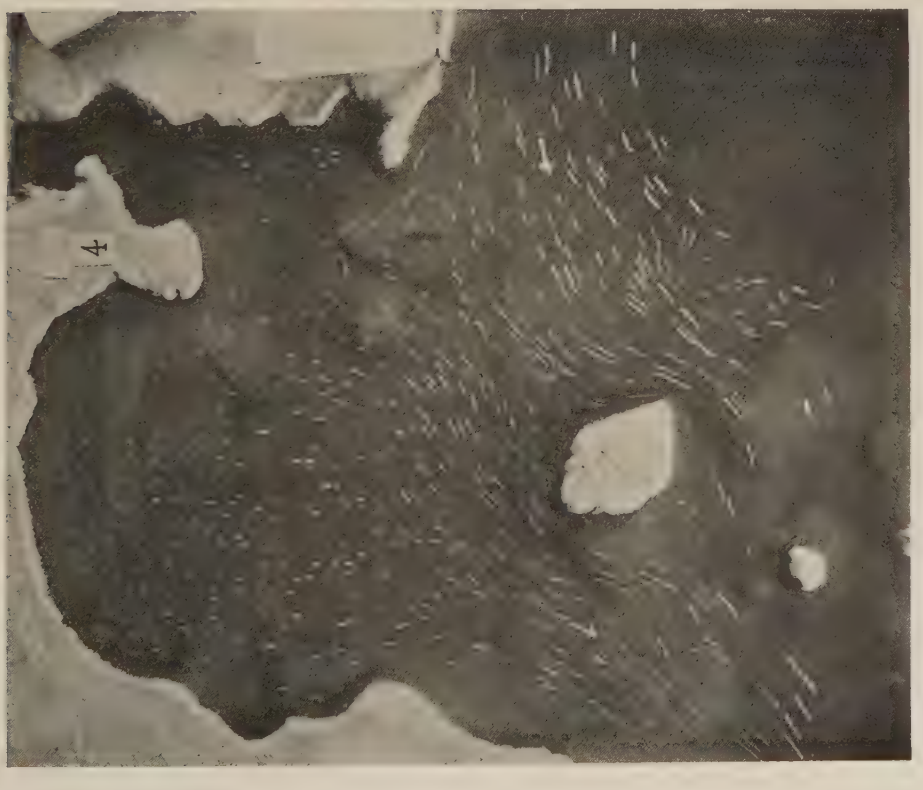




Pl. VI.



Pl. VII.



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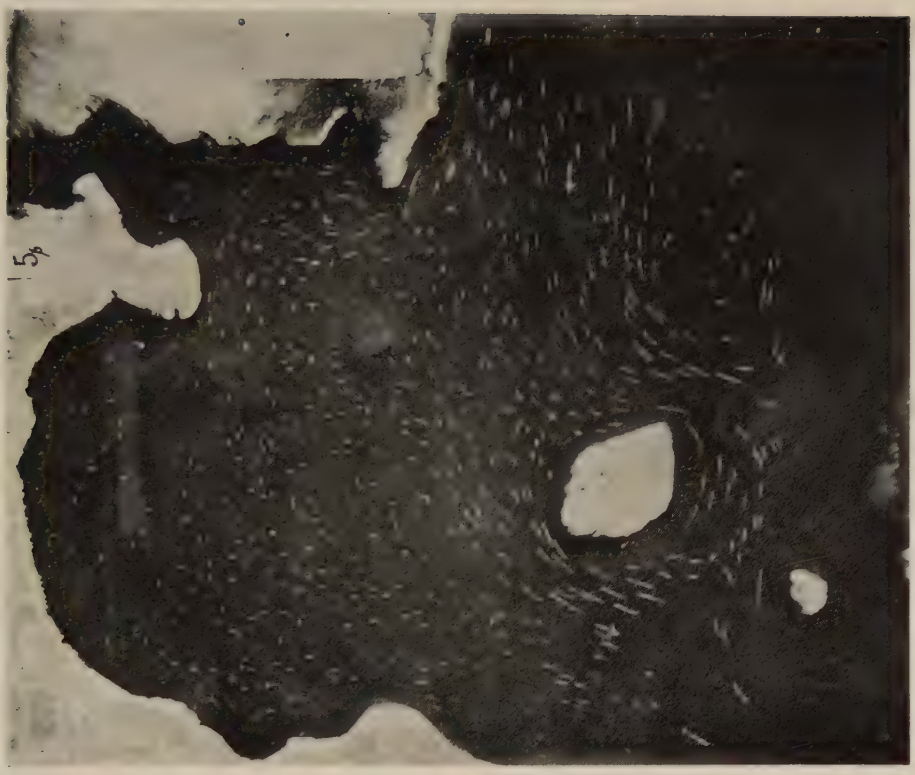

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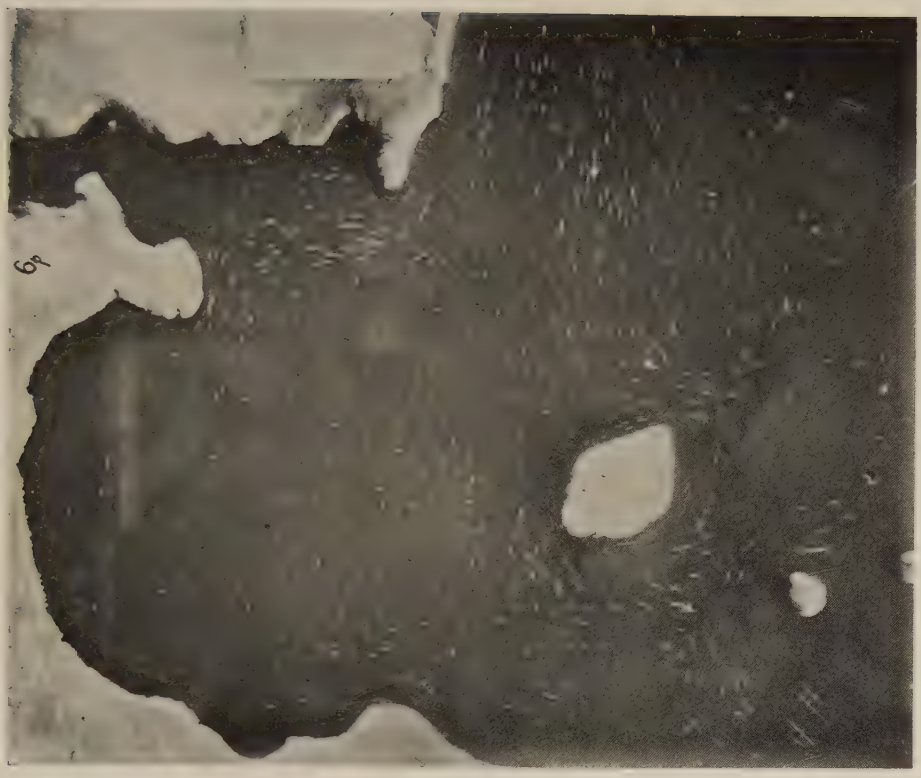

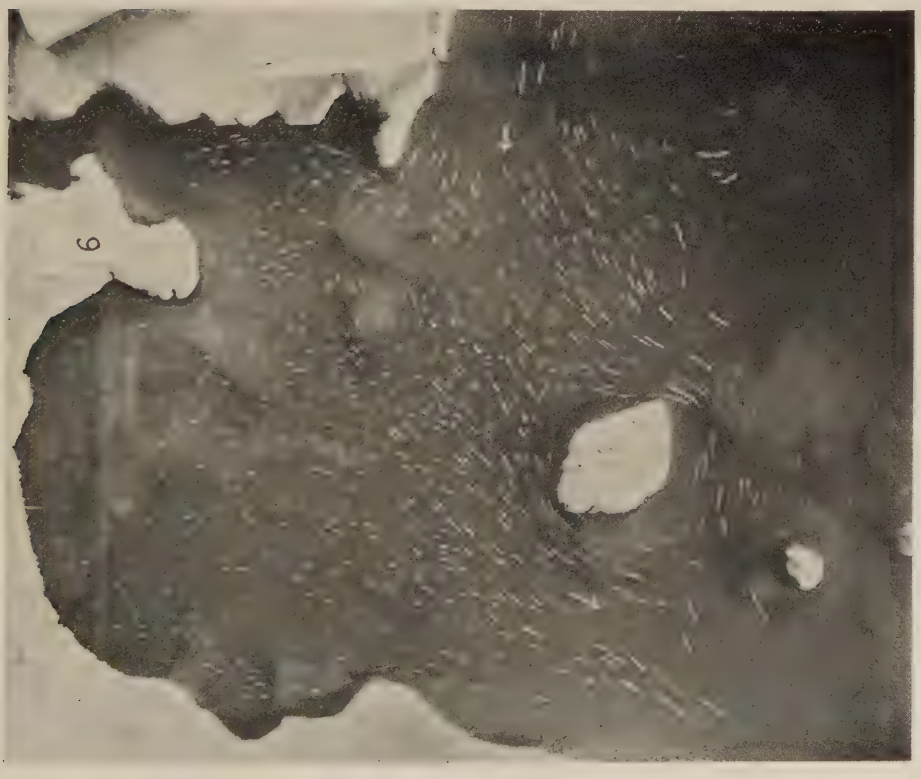

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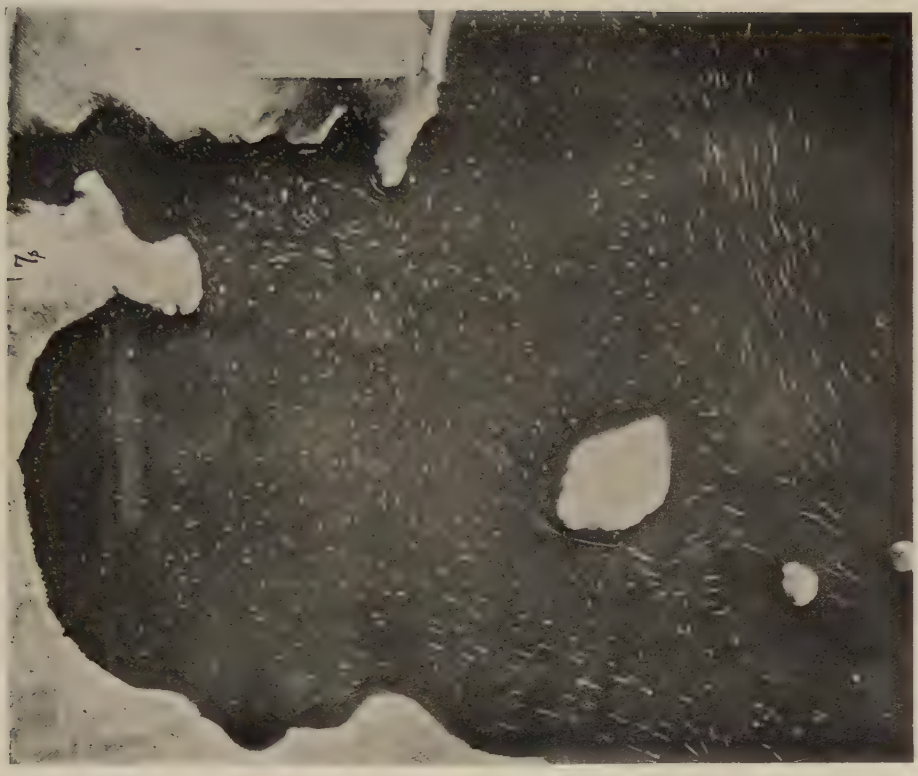

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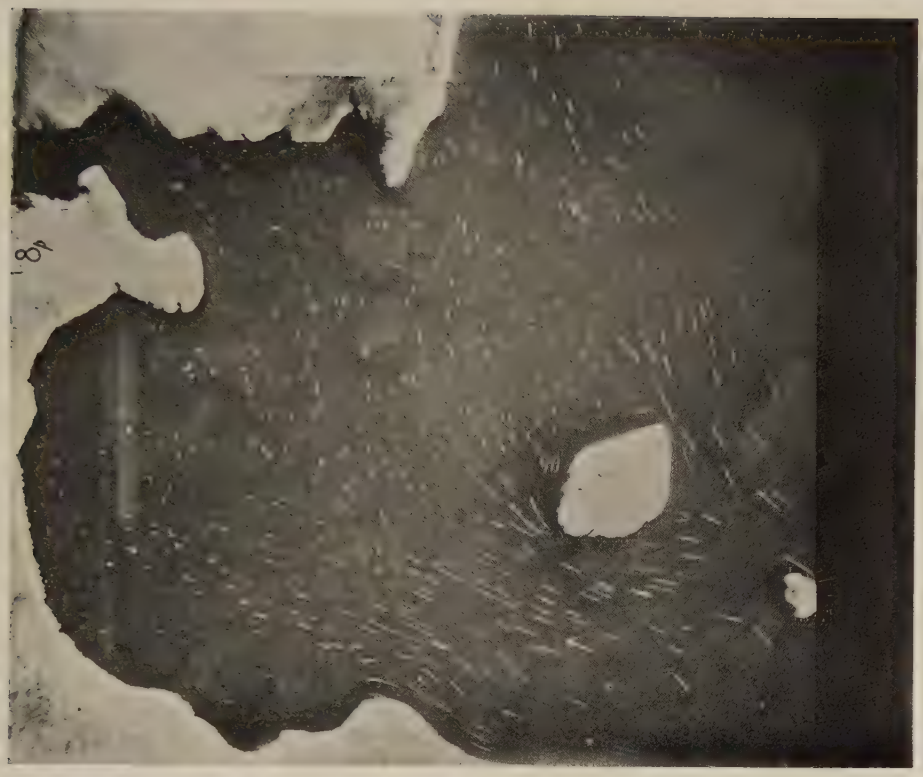

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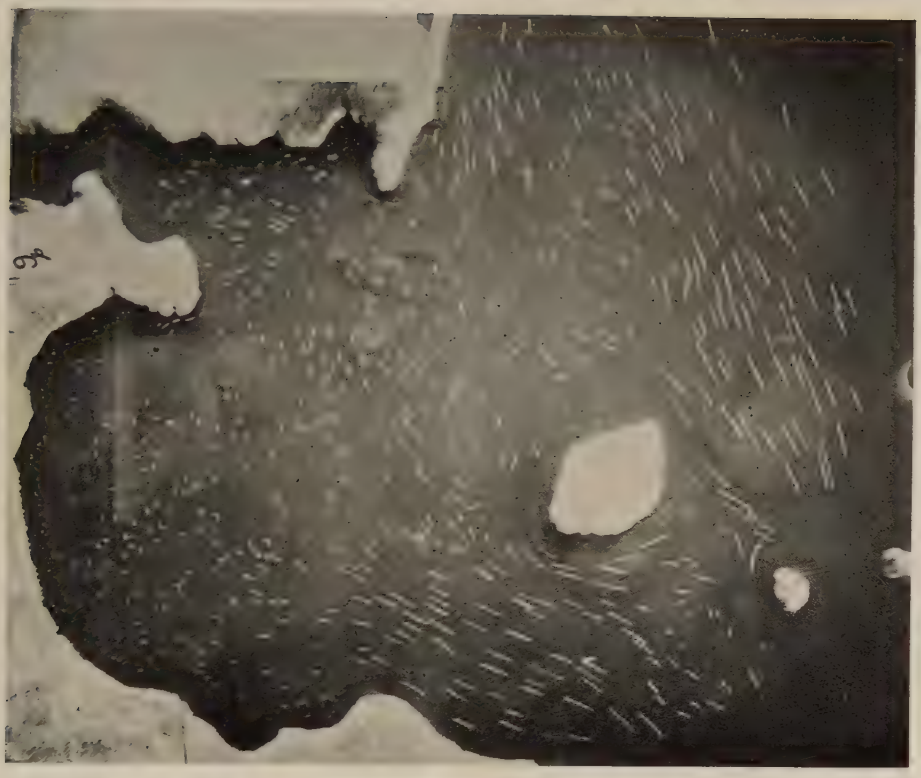

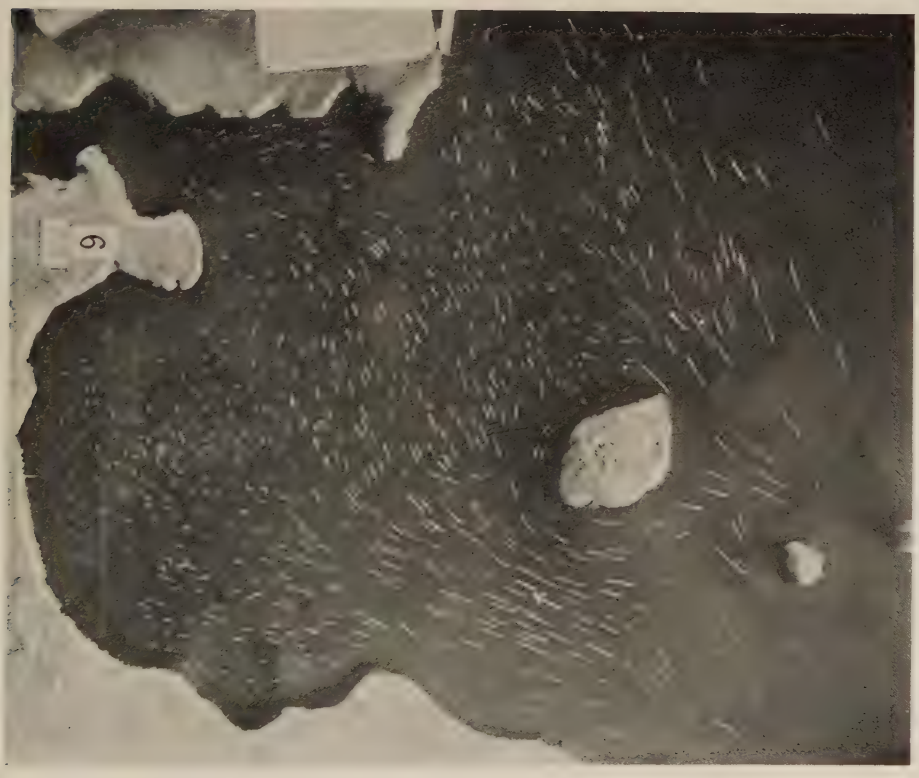

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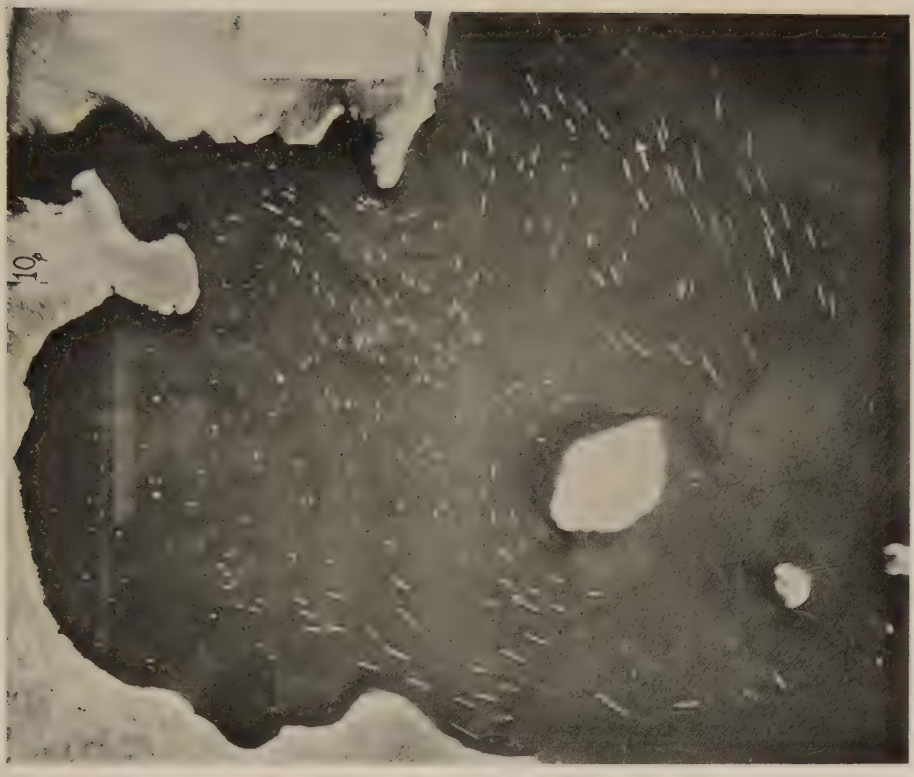
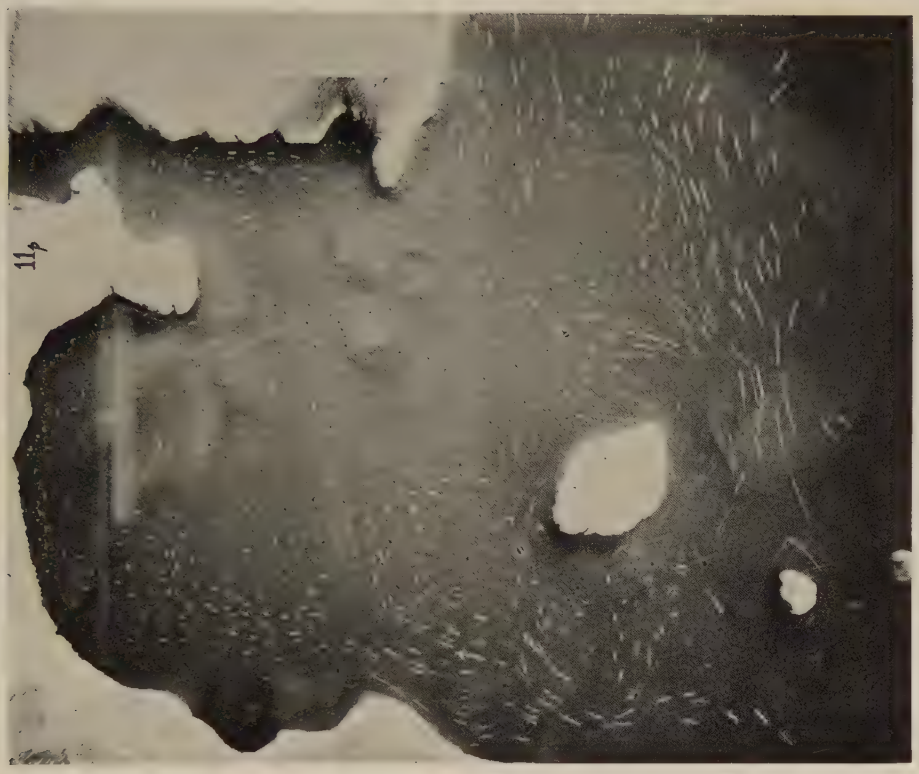


Pl. XIV.



Pl. XV.

On the Stick Antimony Electrode for the Determination of pH.

Tetuo Tomiyama

(Received October 28, 1933)

Introduction

The usual electrometric method with hydrogen electrode or quinhydrone electrode for the determination of pH does not answer the purpose of automatically recording the changing pH of culture media for a long while, since the equilibrium of carbonic acid carbonate system would be disturbed by passing hydrogen through the solution in the former case, and it is necessary to dissolve continuously expensive quinhydrone in the latter case. With a view to investigating the effect of pH on the growth of plankton in a pond or aquarium, a study of the method for measuring pH was undertaken first of all.

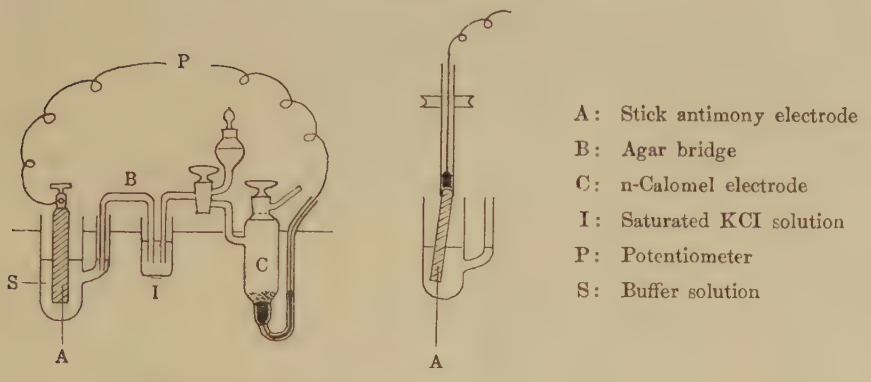
For such a self-recording purpose, the antimony electrode has been frequently used in the industrial line, but the existing results cannot be said to be accurate. Up to the present time, much study has been made of the antimony electrode, especially of the stick type one. Kolthoff and Hartong (1925), Vlès and Vellinger (1927), Franke and Willaman (1928), Snyder (1928), Itano (1929, 1930), Galvez (1930), Parks and Beard (1932), Uemura and Sueda (1933) are the chief investigators. But the results obtained by the different authors do not agree well, and as will be stated later in more detail, this lack of concordant results may be explained by the differences in the procedures used. Kolthoff and Hartong, Britton and Robinson (1931) determined the electrode potential in the solution to which some antimony trioxide had been added. Franke and Willaman, Snyder, Itano, Britton and Robinson, on the one hand, adopted the method of measuring potential while the sample solution was moved by a stirrer or bubbling, or by shaking the sealed electrode vessel. On the other hand, Parks and Beard, Uemura and Sueda studied the relation between pH and E. M. F. with the electrode in unstired solution in contact with air. Different empirical formulae have been given by numerous investigators but generally they do not fit Nernst's formula, as is seen from the following comparison.

Kolthoff and Hartong (1925)	$E = 0.0415 + 0.0485$ pH (pH 1–5 at 14°C.) $E = 0.009 + 0.536$ pH (above pH 8 at 14°C.)
Lava and Hemedes (1928)	$E = 0.052 + 0.057$ pH
Franke and Willaman (1928)	$E = 0.050 + 0.054$ pH at 25°
Harrison and Vridhachalam (1929)	$E = 0.0234 + 0.0498$ pH at 30°
Itano (1929)	$E = 0.017 + 0.054$ pH at 18°
Britton and Rorinson (1931)	$E = 0.018 + 0.0534$ pH
Parks and Beard (1932)	$E = 0.030 + 0.05915$ pH at 25°
Uemura and Sueda (1933)	$E = -0.007 + 0.538$ pH
The writer	$E = 0.022 + 0.0567$ pH at 20°

Therefore, the present author has investigated systematecally some factors governing the electrode potential, using the stick type electrode which has advantages over several other types in being sturdy and easy to prepare. This paper deals with the difference of potential between a stationary and a shakiug state of the electrode, the degree of stability of potential in the stationary state at different temperatures, and the effect of sodium chloride on the electrode potential. From the data obtained, some explanations and criticism also are given of the divergency of the results obtained by different workers.

Experimental Method

Apparatus. For the present investigation, the set of apparatus illustrated in Fig. 1, (a) was used and the potential difference between antimony electrode and n-calomel electrode was measured by a portable PPP-potentiometer (Shimadzu Seisakusho Ltd.), connected with the needle galvanometer, having a sensibility 10^{-8}. Therefore, the accuracy of the present investigation would be in the neighbourhood of ± 0.5 mv. All these measurements were carried out, immersing both electrodes in a thermostat.



(a) (b)

Fig. 1.

Preparation of Stick Antimony Electrode and its Preliminary Treatment. In a part of the experiment, the stick antimony electrode sold by Shimazu Seisakusho Ltd. was used; but as the mode of its preparation was somewhat ambiguous, the author prepared several electrodes which had a difference in cooling rate of the Merck's antimony molten in a pyrex glass tubing as indicated in Table I.

Table I.

Notation of electrode	Mode of preparation
F 1	Metallic antimony fused in an electric furnace is poured in a glass tube and then left to cool gradually at room temperature.
F 2	After casting in the same manner as mentioned above, this is cooled very gradually from fused point to room temperature leaving it in an electric furnace.
D 2	The metal with which the glass tube is previously filled is fused by holding it horizontally on a Bunzen burner, then left to cool at room temperature.
FS	The antimony fused in the same way as F 1 is suddenly cooled by dipping in cold distilled water.

The electrodes were polished with fine emery cloth; then, in order to cover the surface of the electrode with a compact film of antimonous oxide,

they were submitted to a preliminary treatment by being left immersed in the buffer solution of pH 11.8 at room temperature for 2 or 3 days. Since the electrode surface freshly polished shows a different colour when immersed either in acidic or in alkaline solution as was noticed by Uemura and Sueda, and since it loses its metallic property if used continuously for some time, the preliminary treatment is to be adhered to always as above and it should be used without polishing to render the surface condition always the same as far as possible.

Buffer solution. Instead of using a series of separate buffer solutions for calibrating the electrodes, the Prideaux-Ward universal buffer mixture containing the same kinds of acid throughout the range, was adopted and the pH's of all buffer solutions were accurately checked up with both hydrogen electrode (pH 7–12) and quinhydrone electrode (pH 2–8).

Experimental Results and Discussion.

Experiment 1.

Difference of Electrode Potential Between a Stationary and a Shaking State of the Electrode.

Harrison and Vridhachalam (1929), Snyder and Itano (1930) pointed out that the potential in a stationary state showed higher values than that in a shaking state of the electrode. Furthermore, from the works already published it seemed to be general that the slope of pH-E. M. F. curve derived from the data obtained in a shaking state of the electrode is smaller than that of the curve derived from the results in the other state.

In order to examine these effects in detail at different pH's, the change of electrode potential was measured during the intermittent rotation of the electrode (sold by Shimadzu Seisakusho Ltd.) which was cemented to a glass tube in an eccentric position (Fig. 1, b), and the results thus obtained are illustrated in Fig. 2, the rate of rotation in this case amounting to about 100 revolutions per minute.

Fig. 2 shows that the direction of change of potential with the passage of time is opposite according to whether pH of buffer solution is smaller or greater than pH 7–8. When pH is smaller than 7–8, the absolute value of potential difference between antimony electrode and n-calomel electrode decreases

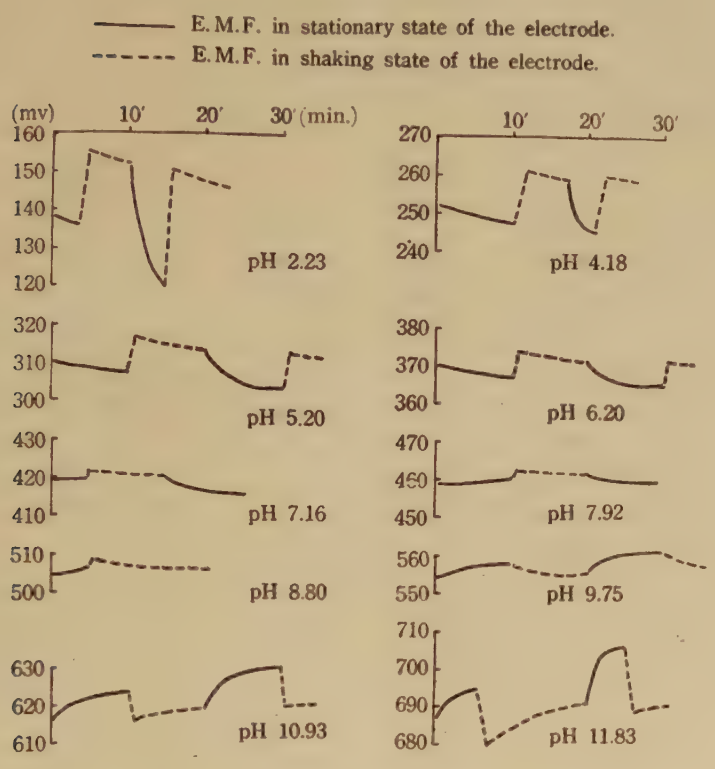


Fig. 2.

Change of potential against n-calomel electrode in stationary state and shaking state of the electrode.

gradually; that is, the positive electric charge of the electrode tends to increase. On the contrary, if pH is greater than 7–8 the above changes are quite the reverse, and the more remote the pH of solution from 7–8 the more these changes are enhanced.

It will be seen also that if the electrode is transferred from a stationary to a shaking condition, a sudden remarkable change in the electrode potential arises particularly in region of pH far remote from pH 7–8. And in the acidic region, the trend of this change is the increasing direction of absolute potential difference, that is, the decrease in positive charge, while in alkaline condition this relation is reversed. From this experiment, it is confirmed that the slope of pH-E. M. F. curve in a stirred condition will become smaller

than that in an unstirred condition when we take the initial value of potential instead of true equilibrated value. Further, since the rate of change in electrode potential is nearly the same, whether in stirred or in unstirred solution, there is perhaps no relative superiority in accuracy between these two conditions.

Experiment 2.

Effect of Temperature upon the Change in Electrode Potential.

It has been noted recently by UEMUKA and SUEDA that the directions of change in potential are dependent upon the pH value of solution, and that the time interval to arrive at equilibrium depends also on the pH value, namely, at about pH 8 it takes a much shorter time to reach equilibrium than at pH far remote from 8. Similar results were obtained, but the equilibrium was never reached in 20–30 minutes as stated by UEMURA in the present experiment, especially in the alkaline side. It might be due partly to the different treatment of the electrode.

So far as the writer knows, there is no detailed investigation as to the effect of temperature on the potential, so that the E. M. F's. of antimony electrode against n-calomel electrode at 10.0°, 20.0° and 30.0°C. were measured during 30 minutes after immersing FS electrode in the buffer solutions. The results obtained are given in Table II and illustrated in Fig. 3.

TABLE II.

pH \ Time-period after immersion (min.)	E. M. F. at 10°			E. M. F. at 20°			E. M. F. at 30°		
	2′	5′	30′	2′	5′	30′	2′	5′	30′
2.23	139	138	136	154	253	152	162	162	162
3.79	224	223	222	241	239	238	254	254	253
5.20	299	298	297	317	315	314	334	334	337
6.20	357	355	353	373	373	373	395	395	397
7.16	406	405	404	423	423	424	447	447	450
7.92	446	449	445	464	465	466	491	492	498
8.80	491	490	489	508	510	511	538	539	547
9.75	536	537	539	559	560	563	589	590	598
11.26	629	633	636	649	652	658	681	683	688

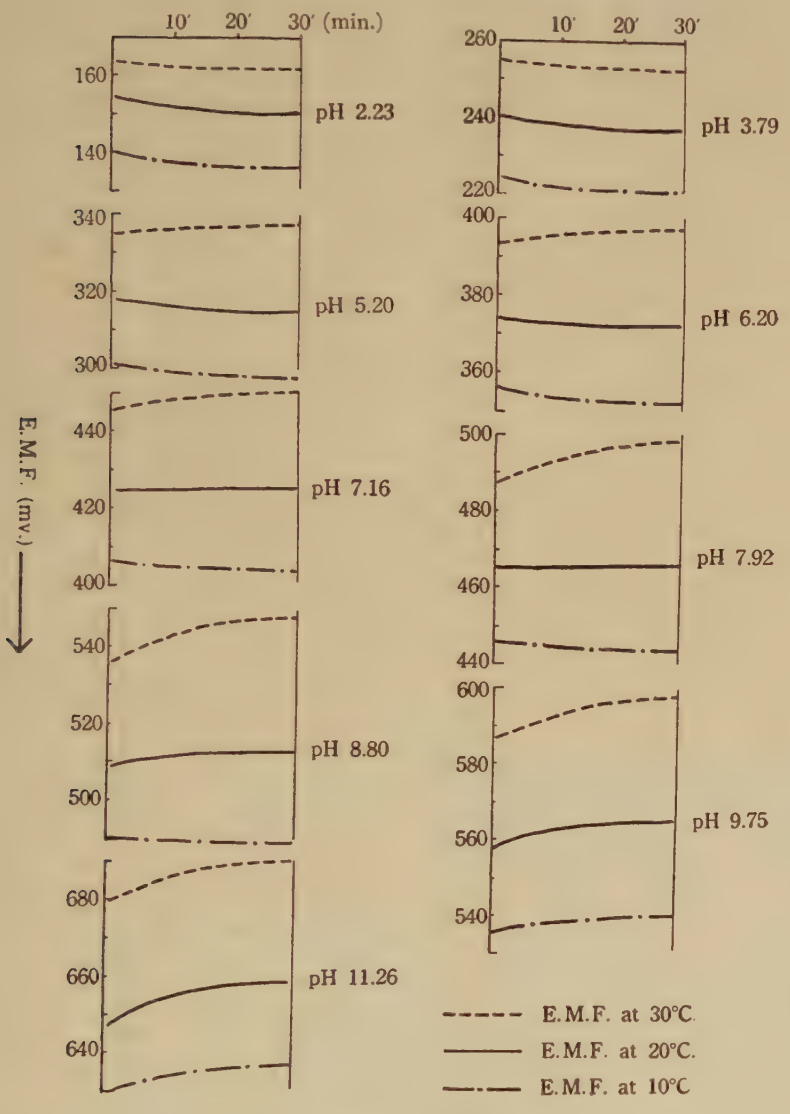


Fig. 3.

The effect of temperature on the change in E. M. F. of antimony electrode against n-calomel electrode.

There is relatively little change in potential at the pH value smaller than 8, whereas on the opposite region of pH, much greater change takes

place for 30 minutes. And increase or decrease in potential until equilibrium is established is not only dependent on pH, but is influenced largely by temperature. From these data, the pH-E. M. F. curves at different temperatures were obtained as seen in Fig. 4, and thus the following temperature coefficients of the electrode were ascertained.

pH of solution	Change in potential in mv. per 1°C.
2–4	1.5
5–7	2.0
8–11	2.5–3.0

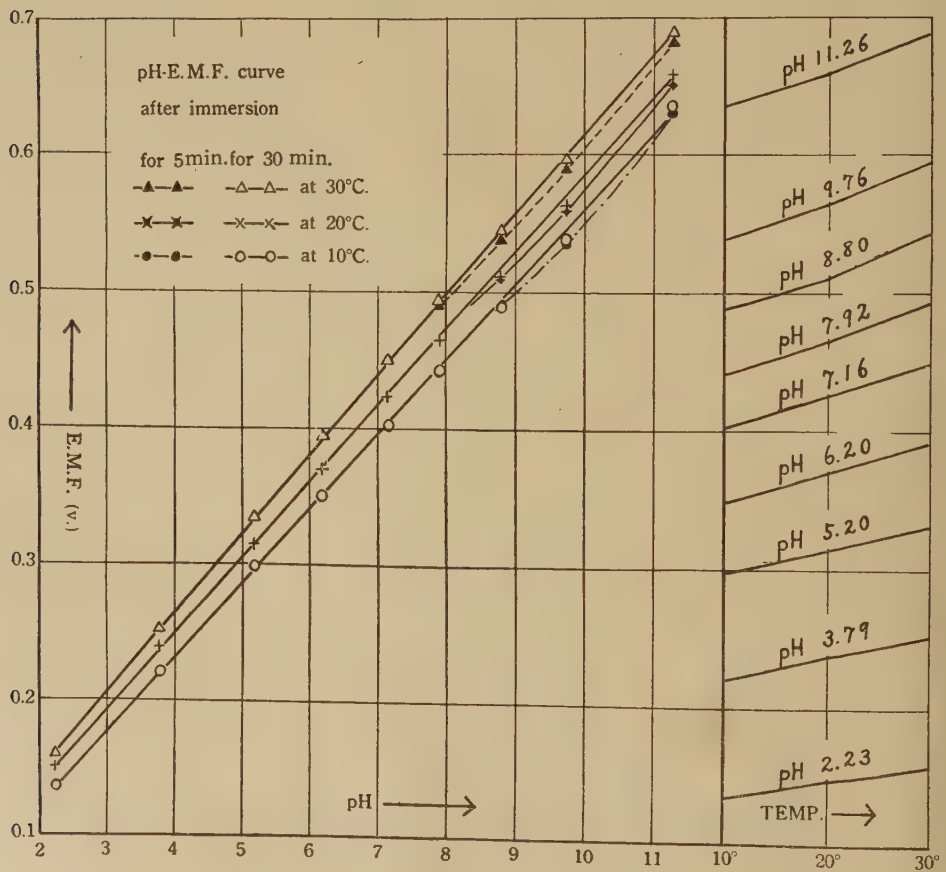


Fig. 4.

pH-E. M. F. curves at different temperatures.

Upon examining the curves of Fig. 4 it will be noticed that if the values observed at a shorter period after immersing the electrode are adopted, marked concave-curve results at the pH greater than 8, and this curve approaches to nearly a straight line at high temperature. In the papers both of PARKS and BEARD and of UEMURA and SUEDA, appreciable deviation from the straight line in alkaline side is clearly observed and consequently it seems to be rather reasonable that the experimental formulae calculated from their results do not coincide with theoretical Nernst formula. For this reason the behaviours of this electrode in different pH's were reexamined for a much longer period in the next experiment.

Experiment 3.

Effect of Time-Period of Immersion on pH-E. M. F. Curve.

The electrodes (F1, F2, D2.) were immersed in the buffer solution at 20°C. and during 150 minutes the change in potential was measured. In no case was complete equilibrium of potential practically established as is shown in Fig. 5.

Fig. 5 indicates that the change in potential in the region of pH above 9.7 is rapid and great i.e. 10-15 mv. per 100 min., while in the region of pH below 7.0 this is very small and gradual, i.e. 3–5 mv. per 100 min. and that in the former case the time to reach nearly equilibrium is within 100 min., whereas in the latter case about 1 mv. per 30 min. continues to change for 2.5 hours. Thus the potential does not readily attain its complete equilibrium value, and so it follows that various experimental formulae can be obtained corresponding to the values at different time intervals. These relations are summarised in Table III.

It is concluded, therefore, that the reason why former investigators have obtained experimental formulae quite different from one another is due to the different conditions under which the measurements were carried out. In consequence, from these experimental data, the author adopted provisionally the values when slope of change dv/dt attained to 1/30, namely change of 1 mv. per 30 min., and from these values (F2 electrode) the pH-E. M. F. curve was obtained as shown in Fig. 6.

In this case there exists nearly a linear relationship between pH and E. M. F., but in the case where E. M. F's. after five minutes' immersion are employed, this deviates from the linear. The values of constants in the three experimental formulae, which were calculated from the nearly equilibrated

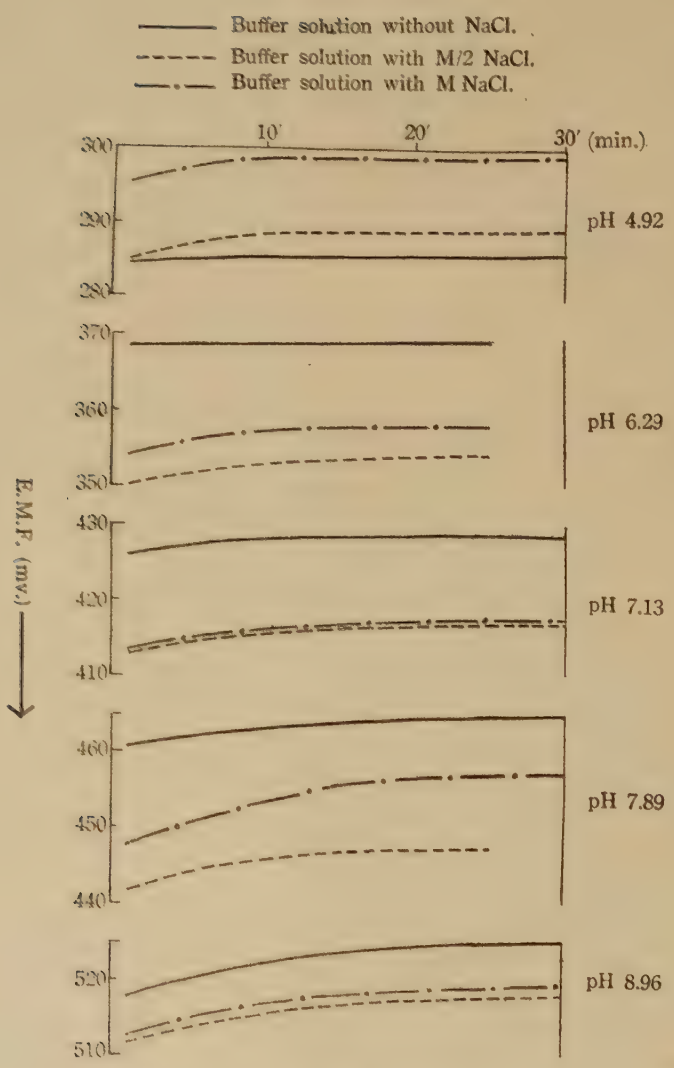


Fig. 5.

Change of E. M. F. during 150 minutes. (F 2.-electrode)

Table III.

E.M.F. / pH	E. M. F. at 5 min. after immerson				E. M. F. when the change of it attains to 1 mv. per 30 min.			E. M. F. at 150 min. after immersion		
No of electrode	F 2	D 2	F 1	F S	F 2	D 2	F 1	F 2	D 2	F 1
Exp. formula	E = 0.030 + 0.0551 pH	E = 0.030 + 0.0549 pH	E = 0.032 + 0.0550 pH	E = 0.031 + 0.0548 pH	E = 0.023 + 0.0566 pH	E = 0.021 + 0.0567 pH	E = 0.022 + 0.0569 pH	E = 0.020 + 0.0569 pH	E = 0.018 + 0.0570 pH	E = 0.020 + 0.0572 pH
	cal. obs.	cal. obs.	cal. obs.	cal. obs.	cal. obs.	cal. obs.	cal. obs.	cal. obs.	cal. obs.	cal. obs.
2.23	153 152 −1	152 151 −1	154 154 0	153 153 0	149 150 +1	147 150 +3	149 152 +3	147 148 +1	145 148 +3	148 149 +1
3.79	239 241 +2	238 241 +3	240 241 +1	239 239 +0	237 239 +2	236 239 +3	238 239 +1	236 237 +1	234 236 +2	237 238 +1
5.20	317 320 +3	316 319 +3	318 320 +2	315 316 +1	317 318 +1	316 315 −1	318 318 0	316 315 −1	314 314 0	317 317 0
6.20	372 375 +3	370 374 +4	373 377 +4	371 373 +2	374 372 −2	373 370 −3	375 373 −2	373 371 −2	371 368 −3	375 371 −4
7.16	425 424 −1	423 423 0	426 426 0	423 423 0	428 425 −3	427 423 −4	429 427 −2	427 426 −1	426 426 0	430 430 0
7.92	467 464 −3	465 462 −3	— — —	465 465 0	471 469 −2	470 470 0	— — —	471 470 −1	469 470 +1	— — —
8.80	515 511 −4	513 510 −3	516 511 −5	513 510 −3	521 518 −3	520 518 −2	523 522 −1	521 518 −3	520 519 −1	523 523 0
9.75	567 561 −6	565 560 −5	568 560 −8	565 560 −5	574 572 −2	574 570 −4	577 573 −4	575 572 −3	574 572 −2	578 573 −5
11.26	650 652 +2	648 648 0	651 652 +1	648 652 +4	660 660 0	659 657 −2	663 660 −3	661 660 −1	660 958 −2	664 660 −4
11.83	682 689 +7	680 688 +8	683 690 +7	— — —	693 698 +5	692 700 +8	696 705 +9	693 698 +5	692 698 +6	697 705 +8

-o--o-- E. M. F. value after immersion of the electrode for 5 min.

—x—x— E. M. F. value when the change of it attains to 1 mv. per 30 min.

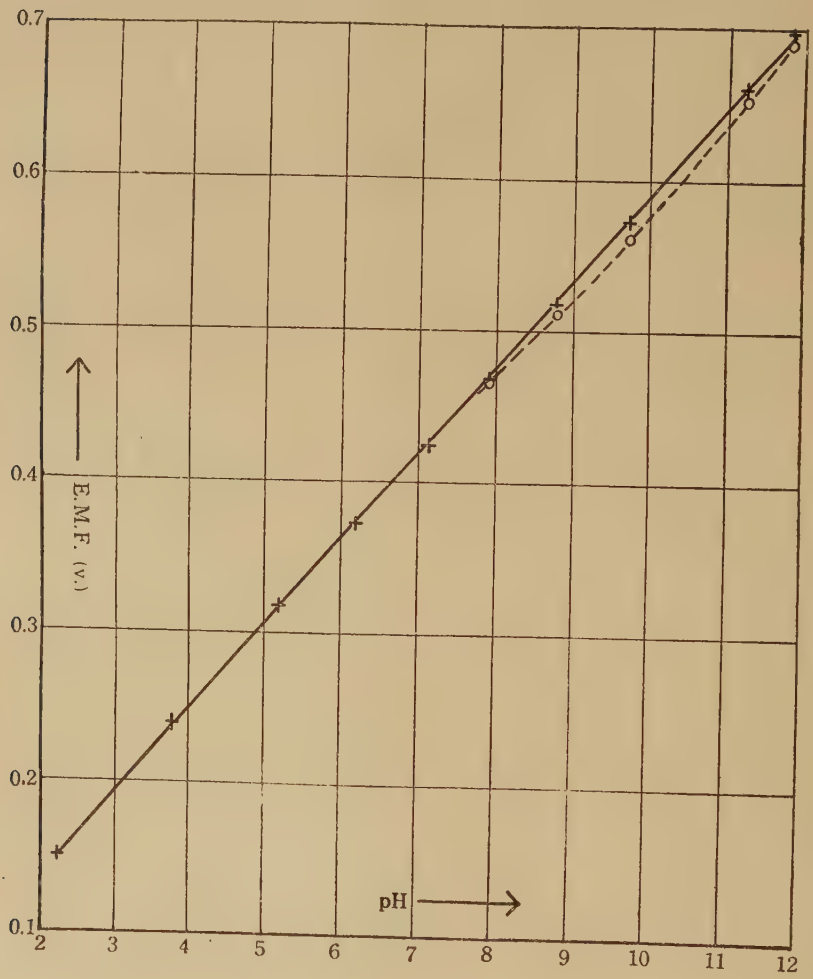


Fig. 6.

pH-E. M. F. curve when the change of potential attains 1 mv. per 30 minutes.

values by the principle of least square, were computed and the following experimental formula was obtained;

$E=0.022+0.0567$ pH at 20°C. against n-calomel electrode.

Experiment 4.

Effect of NaCl on the Electrode Potential.

It is easily supposed that the strong electrolyte affects not only the hydrion activity but would exert a specific influence upon the electrode especially such as a metal-metal oxide electrode. There is no study hitherto of such a salt effect upon the antimony electrode, and so the influence of sodium chloride upon the electrode potential was thoroughly investigated over the range of pH 5–9, with a view to applying this electrode to the measurement of pH of sea water and also ascertaining the fuller knowledge of the chemical behaviour of this electrode.

The potential was measured dipping the electrodes (F2. and D2.) in the following buffer solution which contains either M or M/2 NaCl. The pH's of these buffer solutions were accurately checked up by both hydrogen electrode and quinhydrone electrode.

	Ratio of mixing	
Universal buffer mixture (M/20)	8	8
5 M NaCl solution (Merck's extra pure).....	2	1
Distilled water	0	1
Concentration of NaCl in the buffer solution:	M NaCl	M/2 NaCl

In this experiment, the measurements were carried out at room temperature ranging from 28° to 30°C. and the saturated calomel electrode was used instead of n-calomel electrode, therefore the corrections of temperature and the difference of reference electrode were applied to the observed E. M. F. and then pH values were obtained using the curve (Fig. 4) from thus corrected E. M. F.

The results obtained were illustrated in Fig. 7 and in Table IV. It is clearly seen that the presence of NaCl influences the electrode so as to change much more its potential as time elapses. Comparing the pH values obtained from the corrected E. M. F. at 30 minutes with the paH values by hydrogen electrode, the former give higher values, namely 0.2–0.4 units at M/2 NaCl and of 0.5 units at M NaCl.

Theoretical Consideration.

It has been considered in the former investigations that the potential of antimony electrode is determined purely by hydrogen ion concentration wheth-

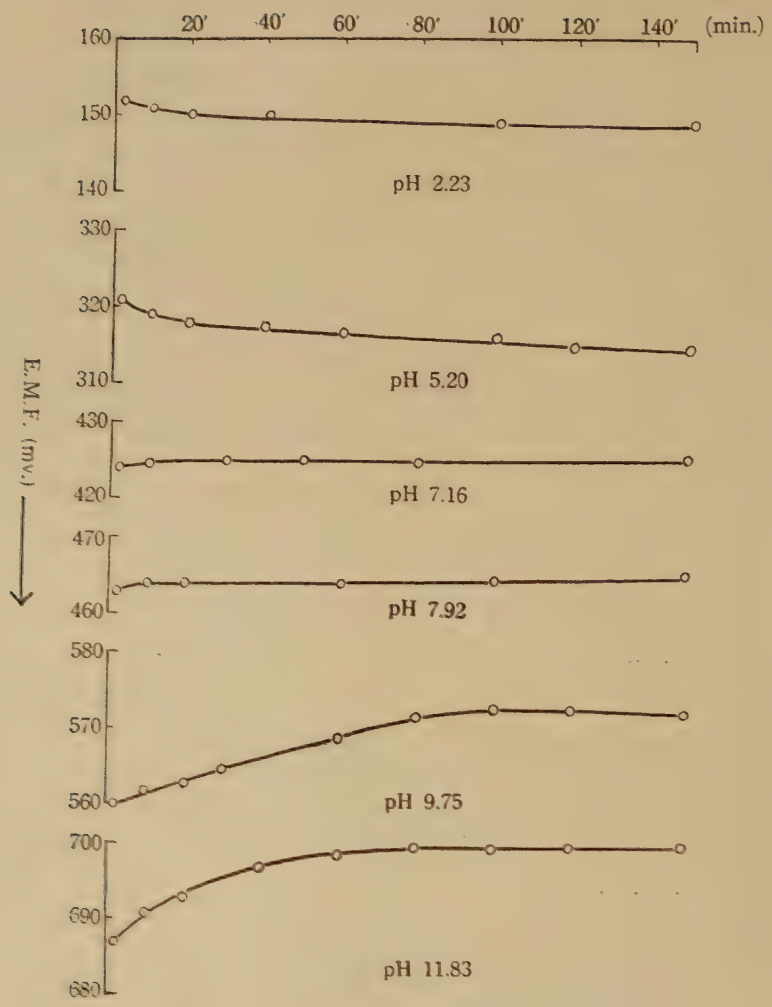


Fig. 7.

er it is immersed in acidic or in alkaline solution. This is theoretically true, but on observing minutely the change in potential and the behaviour of electrode in different pH's. the following consideration, based on the results of the above experiment, may be accepted so as to interpret the nature of the electrode and the mode of creation of potential.

TABLE IV.

Concentration of NaCl in Buffer Solution (Molality)	paH by Hydrogen Electrode	pH by Quinhydrone Electrode	pH by Antimony Electrode
0	4.92	4.88	4.90
½	4.67	4.69	5.00
1	4.61	4.65	5.20
0	6.29	6.28	6.30
½	5.77	5.82	6.17
1	5.62	5.66	6.10
0	7.13	7.13	7.23
½	6.59	6.79	7.20
1	6.76	6.64	7.20
0	7.89	6.87	8.00
½	7.54	7.64	7.77
1	7.37	—	7.90
0	8.96	—	9.10
½	8.71	—	9.00
1	8.57	—	—

Since the antimonous oxide which is formed on the metal electrode has an amphoteric nature, it behaves as acid or base according to the pH of the solution in which the electrode is immersed, as will be seen in the following equation.

$$Sb_2O_3 + 3\,H_2O \rightleftarrows 2\,Sb(OH)_3 \quad \text{.....(1)}$$

$$Sb(OH)_3 + 3\,H^+ \rightleftarrows Sb^{+++} + 3\,H_2O \quad \text{.....(2)}$$

$$Sb(OH)_3 + 3\,OH^- \rightleftarrows SbO_3^{---} + 3\,H_2O \quad \text{.....(3)}$$

In the acidic side of the isoelectric point, antimonous oxide gives off electrons to the hydrion in accordance with equation (2) forming antimony ion and water molecule and consequently positive charge at the electrode increases as much as there exists more hydrion. In the alkaline side, on the contrary, reaction between the oxide and hydroxylion takes place according to equation (3), thus increasing negative charge at the electrode. Hence the change in the electrode potential with the passage of time is perhaps dependent in acidic side on the speed of reaction of the oxide with hydrion and in alkaline side on the speed of reaction with hydroxylion. In consequence, if

both speeds of chemical reactions are the same, the linear relationship will come to hold between pH and E. M. F. in every pH as well as at any time interval according to the equation, $E=E_0+\frac{RT}{F}\ln [H^+]$; but if there is any difference between both speeds, the linear relationship will not be held on both sides of the isoelectric point at definite time interval. Thus the diviation of pH-E. M. F. curve from the linear (Fig. 6) is understood to be due to mainly the irregular speed of reaction above pH 8.

By the above consideration, the direction of change of potential with the passage of time is clearly explained. Now immerse the electrode in acidic solution, and reaction of equation (2) will proceed until it reaches equilibrium, increasing in this way positive charge at the electrode, so that the potential difference between the electrode and the n-calomel electrode, which is more positive than the former, decreases gradually as is seen in Fig. 2 (pH 2.2–7.1). In the case of shaking electrode in acidic side, the surface of electrode immediately after shaking will come into contact with a new phase which does not yet contain sufficient amount of Sb^{+++} for equilibrium, and for this reason the electrode potential moves back to its initial value. And next, with the progress of the solution of the oxide, the potential shifts to positive side, namely it comes to decrease the potential difference against the n-calomel electrode. On the other hand, if the electrode is immersed in the solution of alkaline side of the isoelectric point, the electrode acts as acid; and quite contrary to the behaviour of acidic side, its potential moves to negative side, thus increasing the potential difference against the n-calomel electrode. This consideration agrees well with the results given in Exp. 2 and Exp. 3. It will probably be concluded from Exp. 2, Fig. 3 that the isoelectric point of antimonous oxide would be appreciably influenced by temperature; and at 20°C. this point is determined to be in the neighbourhood of pH 7–8.

As regards the salt error of this electrode shown in Exp. 4, enough explanation cannot be made now until the behaviour of this electrode towards other strong electrolytes comes to be evident in the future work. The irregular phenomenon of the electrode that it behaves as if it were dipped in alkaline solution at pH 5–7 in the presence of NaCl, is due mainly to the effect of temperature shown in Fig. 3. Further, as is seen from the curve in Fig. 7, it seemed that the isoelectric point of the antimonous oxide also might shift to acidic region by the presence of NaCl. This phenomenon might be assumed as analogous behaviour to that of protein ampholyte towards strong electrolyte.

As is considered above in detail, the amphoteric nature of the oxide

certainly plays a fundamental rôle in the creation of potential, and it is concluded that the change in potential as shown by experiments cannot be avoided by any possible improvement so far as such amphoteric nature is concerned and also that to obtain reproducible results it may be essential to cover the electrode by a stable modification of the oxide.

Summary.

1. Factors governing the potential of stick antimony electrode such as shaking the electrode, temperature, time of immersion, presence of NaCl and their bearing on pH-E. M. F. curve have been studied.

2. The electrode which had been coated with antimonous oxide by treating with buffer solution of pH 11.8, showed slight change in its potential if immersed in acidic solution, while a fairly remarkable change was observed in alkaline solution. Although these changes became smaller and smaller as time elapsed, no complete equilibrium was attained during 150 minutes in any case.

3. When the electrode immersed in unstirred solution is shaken suddenly, change in potential against n-calomel electrode takes place in such a way as to increase in acidic solution and to decrease in alkaline solution.

4. In unstirred condition, the experimental formula varies, depending on such factors as temerature and time of immersion. The longer it is immersed in solution, the nearer the pH-E. M. F. curve comes to the straight line. If the E. M. F. after five minutes' immersion is taken, this curve comes to deviate from the linear especially in alkaline side. These anomalous behaviours can be explained by assuming that the potential is created by reaction of the amphoteric oxide with either hydrion or hydroxylion.

5. Temperature coefficient of electrode potential varies according to the range of pH and also according to the time interval of immersion in solution. At 30 minutes after immersion, the following values were ascertained between 10°C. and 30°C.

pH of solution	Change in potential difference per 1°C
2–4	1.5 mv.
5–7	2.0 mv.
8–11	2.5–3.0 mv.

6. By adopting the values of potential when the change attains to 1 mv. per 30 minutes instead of true equilibrated ones, the following experimental formula was obtained in the present investigation.

$E = 0.022 + 0.0567\,pH$ at 20°C., against n-calomel electrode.

7. The presence of NaCl exerts a remarkable effects on the potential of the electrode and the more concentrate NaCl in solution the more remarkable this effect. If the buffer solution contains M/2 NaCl, pH values obtained by antimony electrode at 30°C. shows higher values of 0.2–0.4 pH units than paH values by hydrogen electrode over pH 5–9, and if the buffer solution contains M NaCl, this electrode gives higher value of pH 0.5.

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References.

Britton and Robinson, (1931): J. Chem. soc., 458.
Franke und Willaman, (1928): Ind. Eng. Chem, 20, 87.
Galvez, (1930): Philippine Agr., 19, 219.
Harrison and Vridhachalam, (1929): Memoirs Dept. Agr. India, 10, 157.
Itano, (1929): Ber. Ohara Inst. landow. Forsch. Japan, 4, 273.
Itano and Arakawa, (1930): ibid., 4, 383.
Kolthoff and Hartong, (1825): Rec. trav. chim., 44, 113.
Lava and Hemedes, (1928): Philippine Agr., 17, 337.
Parks and Beard, (1932): J. Amer. Chem. Soc, 54, 856.
Snyder, (1928): Soil science, 26, 107.
Uemura and Sueda, (1933): Bull. Chem. Soc. Japan, 8, 1.
Vlès and Vellinger, (1927): Arch. phys. biol., 6, 38.